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PYRITIC SYSTEMS: A MATHEMATICAL MODEL

Arthur H. Morth, et al

Ohio State University

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Pyritic Systems: A Mathematical Model

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Morth, A~~rthur~~ H.
Smith, E~~dwin~~ E.
Shumate, K~~enesaw~~ S.

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27 Abstract

A mathematical model of an acid mine drainage system has been developed for underground mines. The model relates the rate of acid formation to the rate of pollution discharge from the system.

The calculational model was developed using a digital computer to simulate an existing mine as the sum of many micro scale mines, each representing a small reactive volume in the system being modeled. The input to the model is a physical and chemical description of the system. Day-to-day simulation requires data on temperature, rainfall, and oxygen concentration at the exposed coal face. The output of the model is estimates of daily acid load and drainage flow, plus monthly and yearly summaries.

The calculational model was based on a carefully described physical model so that a predictive model can be constructed with little or no experimental data. However, methods for constructing the computational model are given which can utilize the field data available to increase the reliability of the model. (EPA abstract)

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Abstractor Dr. Edwin E. Smith

Institution The Ohio State University Research Foundation

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PYRITIC SYSTEMS: A MATHEMATICAL MODEL

By

Arthur H. Morth
Edwin E. Smith
and
Kenesaw S. Shumate

Contract No. 14-12-589
Project 14010 EAH

Project Officer

Dr. James M. Shackelford
Pollution Control Analysis Branch
Environmental Protection Agency
Washington, D.C. 20460

Prepared for

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ABSTRACT

A mathematical model of an acid mine drainage system has been developed for underground mines. The model relates the rate of acid formation to the rate of pollution discharge from the system.

The calculational model was developed using a digital computer to simulate an existing mine as the sum of many micro scale mines, each representing a small reactive volume in the system being modeled. The input to the model is a physical and chemical description of the system. Day-to day simulation requires data on temperature, rainfall, and oxygen concentration at the exposed coal face. The output of the model is estimates of daily acid load and drainage flow, plus monthly and yearly summaries.

Acid removal kinetics were related to three removal mechanisms: (1) leaching by water trickling downward through oxidized pyritic material, (2) flushing of oxidation products by movement of the water table, and (3) diffusion of oxidation products by continuous oxidation and adsorption of moisture.

The calculational model was based on a carefully described physical model so that a predictive model can be constructed with little or no experimental data. However, methods for constructing the computational model are given which can utilize the field data available to increase the reliability of the model.

Underground mines for which drainage data were available were modeled to test the ability of the model to predict flow and acid load data from different mines. The model accurately predicts yearly flow and acid loads and duplicates seasonal patterns.

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SECTION I

CONCLUSIONS

1. A mathematical model has been developed which can be used to predict drainage flow rates and acid loads from an underground mine.

2. Basic scientific principles and laboratory data can be used to develop a quantitative model of a natural pyrite oxidation system.

3. The oxidation of pyrite within a natural pyritic system can be accurately described beginning with fundamental kinetic equations for the chemical reactions and transport of oxygen. The major difficulty in obtaining accurate short-term predictive capabilities is in describing the removal mechanisms.

4. The computational model was developed from a carefully described physical model of an underground pyritic system, thereby permitting derivation of a computational model from geologic-hydrologic features only. With this capability, the influence of new mines and effects of different mining procedures on a watershed can be predicted.

5. Although it is possible to complete the computational model without the benefit of field data, the reliability of the model can be greatly increased with only a few representative flow and acid load data.

6. Methods for utilizing field data to increase reliability of the model are available. The more comprehensive the field data, the more reliable the model can be made.

7. The model can predict yearly flow and acid load data within ± 10 percent when field data are available. The general pattern of daily flow and acid load observed is also predicted.

SECTION II

RECOMMENDATIONS

Monitoring of the mine and auger holes in the McDaniel's research complex should be continued. McDaniels mine has been under nitrogen for more than 2 1/2 years and has now reached the point where 90% of the oxidation products stored under equilibrium condition (in air) have been removed. A step change in oxygen concentration, together with careful monitoring of drainage, would permit an independent analysis of removal mechanisms.

Other underground mines, for which flow and acid load data are available, should be modeled using the techniques described in this report. The generality of constants used in the mathematical expressions for calculating flows could be determined, or the effect of geological parameters on these constants could be evaluated.

The effect of changing the form of the ADD equation on the predictive capability of the model should be investigated. A linear relationship between ADD (the water leaving the soil layer per day and going to underground storage) and WOVERW (the ratio of water in the soil layer to the water content at saturation) was assumed. An exponential form, where ADD increases markedly as WOVERW approaches unity (as soil layer approaches saturation) would give more rational HEAD vs. TANK relationships.

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SECTION III

INTRODUCTION

The natural formation of acid as a by-product of mining operations has been observed throughout the world. This acid has been formed by the reaction of oxygen and water with sulfur-bearing minerals, such as pyrite (FeS_2).

The formation of sulfuric acid from pyrite has become a major problem in the coal mining areas of the eastern United States, particularly Ohio, West Virginia, and Pennsylvania. The formation of an acid discharge, popularly known as "acid mine drainage," or simply AMD, is responsible for ruining many streams and lakes as recreation areas, for numerous fish kills, and for general wasting of natural resources and beauty. The acidity also causes corrosion of bridge piers, locks, boat hulls, and pumps.[30]

The acid mine drainage problem has been attacked from many angles, ranging from treatment of acid water and sealing of abandoned mines to laboratory scale research. Research on AMD has included studies in the areas of chemical kinetics, microbiology, mineralogy, geology, hydrology, and treatment methods. Thus far most work has been confined to specific areas with little interaction among disciplines. To coordinate this diverse information, researchers at The Ohio State University have undertaken a systematic analysis of acid mine drainage. The object of the analysis is to develop a mathematical model of acid mine drainage systems.

A useful mathematical model must quantitatively relate the physical and chemical parameters of a pyritic system to the rate of pollution discharge across the boundaries of the system. Such a model would accurately predict the long-term effects of mining operations, abatement procedures, and other conditions imposed on the system.

Of equal importance is the ability to predict surges and peak flows of acid. In many pyritic systems, "normal" runoff can be absorbed without effect on receiving streams. It is the heavy slugs of discharge that periodically cause extensive damage to receiving waters. Prediction of these would allow design of protective neutralizing systems.

The development of a mathematical model of a system usually follows a step-by-step approach. The first step is the identification of what is known about a system (and by inference, what is not known). This may be done by reviewing the literature and work of previous investigators. The second step is filling in the gaps in existing knowledge. The preferred technique is experimentation; however, if the problem is not amenable to experimental solution, approximations can be generated starting from basic scientific principles. The final step is comparing the model behavior with that of the real system. At this time, variables

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are free to interact, and the validity of the basic assumptions is proved or disproved. Once the model has been refined and can predict previous data, then it is possible to forecast the effects of perturbations imposed on the system.

Such a step-by-step procedure will be followed in developing a model of a pyritic oxidation system. In this case, the examination of existing knowledge includes reviewing both general acid mine drainage literature, and experimental studies of natural pyrite oxidation systems. The experimental work is reported along with numerical computation techniques used to evaluate undefined quantities.

Next, the actual model and computational methods are developed and proved, based largely on information from a specific mine. Then the model is evaluated for generality by applying it to other underground pyritic system.

SECTION IV

LITERATURE REVIEW

HISTORICAL

The problem of acid production in coal mining regions has been the subject of studies since before 1900. The earliest studies were essentially reports of local acid production and high acid concentrations in streams after heavy storms. The reports frequently traced the acid source back to abandoned coal mines, and more specifically to iron pyrite associated with the coal. In some manner, the pyritic sulfur was reacting and oxidizing to form sulfuric acid and iron sulfate.

Early attempts were made to stop this oxidation by using mine sealing techniques. This was done with some success in the 1920's in West Virginia, but in other states records of methods and results have been lost. Moulton[26] has presented a good review of the early studies in Ohio.

Since 1965, Bituminous Coal Research, Inc.[21] has issued annual bibliographies of acid mine drainage. The next step beyond reporting of acid production was experimental laboratory work starting as early as 1926. Some of the earlier investigators include Burke and Downs,[6] and Nelson, Snow, and Keys.[28]

OXIDATION MECHANISM

In recent research, the emphasis has been on solution chemistry and the definition of the precise oxidation mechanism. Birle,[4] Kim,[16] Jutte,[15] and Morth[23] studied the basic kinetics of the oxidation of concentrated pyritic material.

Birle[4] performed a general study of the oxidation of iron pyrite. He measured relative surface areas of different structural forms of pyrite. Sulfur ball material of the type found in coal had much greater surface area per unit weight than did highly crystalline museum grade pyrite (fool's gold). In parallel work Stiles[41] showed that the reactivity of pyritic material is proportional to its surface area.

Kim[16] studied the oxidation kinetics of concentrated pyritic material in liquid and vapor phase reactions. The liquid or vapor referred to the phase being recirculated through a pyrite bed. He found that the oxidation rate depended on oxygen concentration. Vapor phase oxidation rates seemed to increase with temperature, but Kim attributed this to the increase in humidity.

Morth[23] also worked with liquid and vapor phase reactions. He found that oxidation rate doubled with a 10°C increase in temperature. He observed that vapor phase oxidation increased with humidity, and that at 100 per cent relative humidity, the vapor phase rate is the same as the liquid phase oxidation rate. Morth suggested that water is both a reactant and a reaction medium.

Jutte[15] studied the influence of oxygen concentration on the oxidation rate. The relative oxygen concentration was controlled by applying nitrogen pressure on a liquid phase oxidation. The oxidation rate decreased with increasing pressure. This result led to the conclusion that there was competition between nitrogen and oxygen for a "reactive site." The concept of a "reactive site" has led research into the area of the actual reaction mechanism in addition to the kinetics or rate of reaction.

ELECTRON TRANSPORT

Singer and Stumm[34]; Smith, Svanks, and Shumate[39]; Smith, Svanks, and Halko[38]; Sasmojo[29]; Grove[14] have studied the electron transport mechanisms of iron pyrite oxidation. Singer and Stumm[34] investigated the liquid phase oxygenation of ferrous ions and the hydrolysis of the resulting ferric ion. They found that sulfate ions retarded the rate of ferrous ion oxidation, and that high surface area materials such as alumina catalyzed the oxidation. They erroneously concluded that (1) ferric ion could not exist in contact with pyrite, (2) the overall rate of pyrite dissolution is independent of the surface structure of the pyrite, and (3) the oxidation rate controlling step is the ferrous iron oxidation.

Smith, Svanks, and Shumate[39] studied the anaerobic (oxygen free) oxidation of pyrite using ferric ion as the oxidant. Working with various ratios of ferric and ferrous ions, Smith et al. concluded that the oxidizing species is a surface-adsorbed ferric ion. The rate-controlling step is the surface transfer of electrons. It was also suggested that aerobic (oxygen) and ferric ion oxidations follow different reaction paths. In a continuation of the above study, Smith, Svanks, and Halko[38] reported that the aerobic oxidation rate was a function only of the oxygen concentration at the reactive site; however, the ferric ion oxidation rate was dependent on the ferric-ferrous ratio and the total iron concentration in solution.

Sasmojo[29] studied the kinetics of both aerobic and ferric ion oxidation and attempted to determine if there was an interdependence between the two reactions. He compared the aerobic oxidation rate in the presence and absence of ferrous ions in solution and found no difference. Then using identical total iron concentration, ferric-ferrous ratios, and pH, Sasmojo measured the ferric ion oxidation rate. This rate was about one-third of the aerobic oxidation rate. He concluded that the rate of pyrite oxidation by oxygen is not controlled by the oxidation reaction of ferrous to ferric ion in solution. Sasmojo studied ferric ion oxidation at varying ferric-ferrous ratios and total iron concentrations. At constant total iron concentration, the rate increased with ferric-ferrous ratio, and at constant ferric concentration, the rate increased with decreasing ferrous concentration. From this, he concluded not only that ferric ions increased the oxidation rate, but that ferrous ions had an inhibiting effect.

Grove[14] also investigated ferric ion oxidation and the effects of the ferric-ferrous ratio. He found that the real variable was the free ferric-ferrous ratio. He defined free ions as those which were not complexed nor associated with the solution anions in any manner. He developed a set of equations to estimate the effects of anions on the free ferric-ferrous ratio.

Smith and Shumate[27] in a final project report have summarized and put in proper perspective the various pyrite oxidation studies performed at The Ohio State University. The time interval covered includes the work of Birle through that of Sasmojo. The report is particularly significant since it is a unified presentation of information from different approaches to the problem of defining the sulfide-to-sulfate reaction mechanism.

MICROBIOLOGICAL OXIDATION

Microbiology has been another area of laboratory scale investigations. Bacteria, such as *Ferrobacillus ferrooxidans*, enhance the rate of pyrite oxidation. Lorenz and Tarpley[20] and Konecik[17] reported 10- to 50-fold increases when these bacteria were added to pyritic systems. Bailey[2] found that bacteria increased the oxidation rate, but only after 70 to 80 per cent of the iron in the reaction medium had been oxidized to the ferric state.

Dugan and Lundgren[12] investigated the metabolism of *Ferrobacillus ferrooxidans*. The organisms were found to use the oxidation of ferrous to ferric ions as their energy source. Hence, the bacterial enhancement of oxidation rate arises from the increase in ferric ions during *F. ferrooxidans* metabolism.

Lau, Shumate, and Smith[19] studied the role of bacteria in the kinetics of pyrite oxidation. They studied the growth of *Ferrobacillus* species in a medium where pyrite was the only source of reduced iron. The bacteria multiplied and increased the rate of pyrite oxidation by maintaining a high (in excess of six) ferric-ferrous ratio in the solution around the pyrite. Lau *et al*. noted the influence of the water-pyrite ratio on the rate of oxidation. For low ratios, the oxidation rate was limited by the number of bacteria in the water while at high ratios there were excess bacteria and the pyrite surface area influenced the reaction rate. They suggested that bacterial catalysis is much more likely at the surface of a pyritic system such as a refuse pile than in an underground mine environment. This is attributed to the fact that oxygen is the ultimate electron acceptor and must be readily available for bacterial activity to occur.

GEOLOGICAL STUDIES

Since acid mine drainage causes stream deterioration not in a laboratory, but in the real world, studies in the earth sciences, geology, hydrology, and mineralogy are as important as laboratory investigations. In such studies, pyrite is not isolated but is distributed in a binder such as coal or shale.

Caruccio and Parizek[8] and Caruccio[7] have conducted extensive investigations of geologic factors in acid mine drainage around Clearfield, Pennsylvania. Two locations were compared, one having acidic strip mine drainage, the other nonacidic drainage. Caruccio and Parizek conducted leaching studies to determine if the acid potential of a coal could be related to its sulfur content. While increased sulfur led to greater acidity, this factor did not explain drainage differences of the observed area.

Caruccio[7] found that finer pyrite grains led to higher acidic activity. He also suggested that shales may generate more acid than coal binders. Coal is relatively "tight" and seals the pyrite from the atmosphere while the relatively permeable shale permits oxidation of the enclosed pyrite. Finally, Caruccio noted that if the ground water in a mining area contains calcium carbonate, alkalinity will develop to counteract acidity. Thus, even if acidic oxidation is occurring, the net effluent will not be acidic.

Vimmerstedt and Struthers[43] studied the weathering of spoils material from Ohio Strip mines. They packed the spoils into columns and exposed these to natural weather conditions. The leachate leaving the bottoms of the columns was collected and analyzed for soluble salts, sulfate, and various cations. The investigators found the the amount of leachate and weight of salts followed the annual rainfall pattern. Through regression analysis it was also determined that there was an overall decrease with time in the weight of salts leached. This simply indicated that the pyrite in the samples was being consumed.

Several investigators have checked the effects of coal mining on the hydrology of an entire water shed. Corbett[10] and Agnew and Corbett[1] have studied the hydrology and chemistry of coal mine drainage in Indiana. In particular, they were concerned with flushouts during storms in strip mined areas. Corbett observed that the refuse piles acted as aquifers to store water during storms; the stored water would then be released gradually during dry weather. On the average, about 30 per cent of a given storm was retained in the heavily mined areas as opposed to 15 per cent retention in less mined regions. The peak stream flow during a storm was also considerably less in the stripped area. Corbett did observe that if the refuse piles were already saturated or if there had been heavy compaction during grading of the mined areas, the surface runoff would be enhanced relative to undisturbed land.

Agnew and Corbett[1] emphasized the need for continuous data when studying flushouts and natural systems. Peak flows occurred over a period of hours rather than days. The flushouts increased the concentration of deleterious ions (sulfate, hardness, acidity, and iron) in the receiving streams from 30 to 1000 per cent over normal levels. These concentrations increased at the start of the storm and remained high even after flows had receded. Agnew and Corbett also suggested that some standard method of reporting acidity be determined. In particular, it seemed that both "acidity" and "alkalinity" should be reported rather than just a net acidity. A number of other questions were raised about the analysis of mine waters.

DISCUSSION

The investigations discussed to this point can be considered no more than a sampling of the total acid mine drainage literature. They are typical of the varying points of view which must be considered in any model of pyritic systems. Although methods and interpretation of results may vary, investigators have well defined the kinetics of iron pyrite oxidation.

The importance of oxygen has been stressed as would be expected in an oxidation reaction. In kinetic terms, the oxidation rate is a fractional order with respect to oxygen concentration. Jutte[15] estimated the dependency as three-fourths power. Over the normal range of atmospheric concentrations this can be taken as a linear (or first-order) dependence.

The rate of pyrite oxidation has been shown to depend more on the pyrite surface available than on the absolute weight of pyrite present. Stiles[41] came to this conclusion for concentrated, crushed, sieved pyritic material. Caruccio and Parizek[8] observed a similar dependence for pyrite still embedded in coal. Their observation was based on a qualitative estimate of the fineness of pyrite grains rather than on exact measurements.

As the stoichiometric chemical reaction equation showed, water is also part of the pyrite oxidation reaction system. Kim[16] and Morth[23] investigated the influence of water on the oxidation rate. In liquid phase reactions, water was present in excess and did not enter the oxidation rate equation. It was only in vapor phase reactions where humidity could be varied that water concentration appeared to influence rates. No specific reason for this influence was put forth until investigations of the actual reaction mechanism were undertaken. The mechanism studies led to the conclusion that water was necessary as an oxidation product dissolution medium. The influence of humidity was then related to how much of the pyrite surface contained adsorbed water and was available as a reaction zone. Hence, for the rate limiting step, the basic function of water is to provide a means for the removal of oxidation products.

The determination of the oxidation mechanism involved not only chemists but also geochemists and microbiologists. Here differences in philosophy and technique tended to cause divergent interpretations of similar experimental data. Singer and Stumm[3] in their studies of liquid phase oxygenation of ferrous ions and dissolution of pyrite, concluded that ferric ions could not exist in contact with pyrite. They also stated that the ferric ion was the only actual oxidizing agent even though oxygen might be the ultimate electron acceptor. The first conclusion perhaps is based on a thermodynamic approach where infinite time is allowed for a reaction to reach equilibrium rather than on a kinetic approach where concentrations are considered as functions of time. There is strong evidence to contradict the conclusion that ferric ions in solution are the only species capable of directly oxidizing pyrite. In studying liquid phase oxidation Morth[23] placed an Amberlite® IRA-120 ion exchange resin bed in series with the pyrite bed in a recirculating solution. No iron was found in this solution using ortho-phenanthroline spectrophotometric analysis. However, the oxidation rate, as measured by oxygen consumption, was the same as in runs where iron concentrations were at the 1000 ppm level.

Smith, Svanks, and Halko[38] also refuted Singer and Stumm by showing that there are parallel oxidation mechanisms whereby oxygen and ferric ions simultaneously and independently oxidize pyrite. In addition, Sasmojo[29] showed a direct surface reaction of pyrite with adsorbed oxygen. Finally, as a practical matter, in a real system there is no recirculation of iron-containing water over the pyrite. In experimental work, iron-containing solutions were contacted with pyrite, and the reduced iron then reoxidized to the ferric state after returning to the bulk solution. In nature, the only way that the reduced iron can leave the oxidation site is by gravity flow. If the water flow is away from the oxidation site, it is improbable that the iron ions, when reoxidized, return to the pyritic surface. This is not to deny the possibility that drainage from one mine could come in contact with pyritic material in a lower elevation mine.

In discussing the two mechanisms of pyrite oxidation Smith and Shumate[27] stated that at low ferric-ferrous ratios, oxygen oxidation is dominant. As the ratio increases, the relative importance of ferric ion oxidation increases until at ratios in excess of five, ferric oxidation is dominant. In a natural system, the only way to reach this ratio is through Ferrobacillus species oxidation of ferrous to ferric ions, since at a pH of two or three the rate of oxygenation of ferrous to ferric ions is too slow to maintain a high ferric concentration in solution. This requirement of bacterial assistance is in accord with Bailey's[2] observation that in a laboratory oxidation system containing Ferrobacillus species, the pyrite oxidation rate increased only after the bacteria had oxidized 70 to 80 per cent of the iron in the reaction medium to the ferric state.

While laboratory investigations were concerned with detailed examination of the oxidation reaction, there have been few detailed studies of what happens once oxidation products have been formed. There is a middle ground such as that taken by Vimmerstedt and Struthers[43] who worked with spoils material. They observed that trickling flow such as that produced by rainfall removes oxidation products. This same observation has been made by nearly everyone who was concerned by acid flushouts after heavy storms. Overall, no great effort has been expended in defining the exact mechanism whereby acid products move from the reaction site to the receiving stream.

Field studies have emphasized that neutralization by naturally occurring alkalinity is as important as the formation of acid. Caruccio and Parizek[8] and Agnew and Corbett[1] reported that calcium and magnesium carbonates neutralize acidic drainage. The difficulty arises in defining how much acid was originally produced at the source. Should just sulfuric acid be included or should the acidity of metallic sulfates such as ferrous or ferric sulfate also be considered? Sulfuric acid is important because of biological effects, but total acidity determines the cost of treatment. Most analytical techniques determine the total acidity by hot titration to a phenolphthalein end point. Agnew and Corbett[1] also observed that if the acid equivalent of hardness was added to the value of measured acidity in their samples, the sum was quite close to the sulfate level. The implication of this equality is that hardness is indicative of neutralized acidity. The only shortcoming of all these calculations is that none considered the effects of precipitation of iron hydroxy sulfates or other metallic sulfates. The main conclusion that can be drawn is that natural alkalinity of ground water should be considered and that hardness may be taken as a good estimate of the alkalinity which had been available.

MODEL ORIENTED STUDIES

While much has been written in the area of acid mine drainage, there are a number of studies of particular importance to the development of a mathematical model of a pyritic system.

Smith[36] laid the basis for the development of such a model by discussing the engineering aspects of acid mine drainage. In particular, he showed how basic laboratory rate data and "first principles" of engineering could be used to estimate acid mine drainage discharge rates.

Basic Concepts of Model

A mathematical model of pyritic systems was first suggested by Shumate, Smith, and Brant[33] in 1969. They expressed the belief that a model would greatly reduce the time and expense of studying acid mine drainage. They described pyrite oxidation within the framework of a basic engineering system in the hope of stimulating critical discussion. Shumate et al. summarized five characteristics common to all pyrite systems which must be considered in any model:

1. The oxidation is a heterogeneous reaction involving crystalline pyrite with oxygen in water. The environment at the reaction site determines the reaction kinetics.

2. Oxygen transport is in the gas phase.

3. Pyrite exposed to a vapor phase will oxidize at a rate similar to pyrite in water, provided the relative humidity is near 100 per cent.

4. Removal of oxidation products has no influence on the rate of oxidation.

5. In general, the reaction does not occur on the bulk surface, but on pyrite embedded in a porous structure.

These five criteria are little more than restatements of the research results already discussed. However, they are indicative of the orderly, logical approach which must be used in the development of a mathematical model of a pyritic system. Shumate *et al.*[33] also suggested methods of relating rates of oxidation, and acid release, to system characteristics. The thrust of the suggestions was to treat a pyritic system as the sum of many micro-systems.

McDaniels Research Complex

There have been two major investigations of natural systems by workers at The Ohio State University. The development of a natural laboratory by Shumate and Smith[31] and the study of a refuse pile by Good[13] have furnished much of the information for development of a mathematical model.

Shumate and Smith have developed the McDaniels Research Complex in Vinton County in southeastern Ohio. The complex, administered by The Ohio State University, includes the McDaniels Test Mine and six experimental auger holes. The mine is located in the extensively mined upper reaches of Sandy Run in Brown Township in the Middle Kittanning (No. 6) coal bed. Moulton[26] has described the geology of the area as follows:

> There is a discontinuous shale layer overlying the coal, but a shaly sandstone is present most frequently. The sandstone, though shaly or silty at the base grades upward into a massive, medium grained, well cemented rock....The sandstone over the Middle Kittanning coal bed is about 40 feet thick, and at its top there is a thin stained zone which indicates the horizon of the Lower Freeport coal....The general character of the remaining upper part of the geologic section is of sandstone or silt composition, with exception of more or less minor occurrences of shale, limestone, and thin clay and coal beds.

In selecting a mine suitable for field research, investigators examined four mines in the Sandy Run area. The McDaniels Mine was selected because it best met the following four criteria:

1. It was physically separated from all other mines.

2. There was only one opening to be sealed.

3. The strata near the opening were sound so that a tight seal could be constructed.

4. The mine produced a significant quantity of acid mine water.

McDaniels Mine was also relatively small and in a good state of repair.

The test mine is a small drift mine extending 35 to 40 feet into the hillside. The refuse and other material left during mining was removed. A concrete seal was placed on the only entrance to the mine. The seal contains sampling ports and connections for injecting gases for controlling the atmosphere in the mine. The geology and hydrology of the mine was determined. Six observation wells were drilled in the hillside above the mine.

The most important aspect of the test mine work has been the continued periodic measurements of drainage flow rates and chemical analyses for more than five years. The data are important both because of their frequency and because they represent a relatively well-defined system. Besides collecting data, Shumate and Smith[31] have attempted to use the mine as one would use a chemical engineering pilot plant to perform experiments.

The main variable available for experimentation was the atmosphere within the mine. Since the mine is located in a "tight" geologic formation and has only one man-made opening, the initial test was simply to put a seal at the entrance. With a seal, the oxygen concentration in the mine atmosphere dropped to 10 per cent, but no lower. This behavior, which has been observed in a number of other "sealed" mines, has been attributed to "breathing." "Breathing" is the pushing and pulling of air through the fine channels in the overburden by atmospheric pressure variations. To counter-act breathing, positive atmospheric control was maintained by injecting gases into the mine to maintain a slight positive pressure relative to the outside atmosphere. The gases that have been injected include oxygen, nitrogen, and air. The oxygen was added to raise the oxygen level. The nitrogen was added to minimize the oxygen level, and air was injected to hold a constant 21 per cent oxygen level.

The expectation of the investigators was that the results of a change in the atmosphere would become apparent in one or two months. This hypothesis was based on the assumption that oxidation was occurring close to water flow channels and that products were washed out soon after formation. It was only after 6 to 8 month delays that anticipated acid load changes occurred. This response lag indicated that oxidation was occurring in areas away from normal flow channels. Product in unleached volumes would only be removed by gravity diffusion as described in Section VI. Hence, no changes in acid removal would be noted until the previously accumulated oxidation products had been removed from the system. In light of this conclusion, the most recent experiment, addition of nitrogen to maintain a slight positive pressure of nitrogen at all times, has been in progress since the middle of 1969. One of the best checks of any model which is developed is that it will show a long lag time similar to the observations at the McDaniels Test Mine. In other experiments, the permeability of the over-burden was estimated, and core drill samples were taken from behind the exposed coal faces. These cores showed that pyrite oxidation had occurred as much as 50 feet into the coal away from the bulk atmosphere.

Six experimental auger holes were drilled in the same coal seam as the McDaniels Test Mine, but on the other side of the valley. The flow rate and drainage characteristics from these holes have been monitored since they were drilled in the summer of 1969. The most notable observation has been the change from alkaline to acidic discharges. The change is a sign of increasing acid production rather than a decrease in the natural alkalinity of the ground water. A publication describing all of the research at the McDaniels Research Complex has been prepared by Smith and Shumate.[37]

In Situ Oxidation Rates

Larez[18] determined the oxidation rates of pyrite contained in natural coal and shale. He obtained blocks of coal and shale from the walls of Auger Hole No. 3 at the McDaniels Research Site. The oxygen uptake rate of each of the blocks was measured in a Warburg-type apparatus. The oxygen consumption for shale was about 3 $\mu g \cdot hr^{-1} \cdot cm^{-3}$ of solid. For the coal binder, the uptake was only 1 $\mu g\ O_2 \cdot hr^{-1} \cdot cm^{-3}$. In engineering units, these rates are in the range from 0.01 to 0.1 pound per day per cubic foot solid. This difference in rates was attributed to the higher pyrite content and greater porosity of the shale. Since the blocks used were only about a centimeter in thickness, the observed rates are probably the maximum possible at the operating conditions used. These rates can be used as boundary conditions in developing a model.

Larez exposed the sample blocks to chlorine to kill any bacteria present. This treatment had no influence on the shale block oxygen uptake rate, and slightly decreased the coal rate to 0.7 $\mu g \cdot hr^{-1} \cdot cm^{-3}$ solid. These results prove nothing concerning the effect of bacteria on acid production and may only indicate the total absence of bacteria.

Refuse Piles

Good[13] has investigated acidic drainage from the refuse pile of the New Kathleen Mine. This mine, near DuQuoin, Illinois, was operated by the Truax-Traer Coal Company. The pile covers an area of about 40 acres and rises 40 to 65 feet above the surrounding farm land. The pile contains about two million cubic yards of coal refuse. Good described the hydrology and oxidation characteristics of the refuse pile.

Oxidation appeared to occur in a 4- to 10-inch thick outer mantle. The clay was washed out of this layer by rainfall to form a layer of clay just beneath the outer mantle. This clay layer was tightly packed and about an inch thick. The layer had low permeability, but there were cracks and crevices where water could enter the main part of the pile. The clay layer did serve as an oxygen and water barrier over most of the pile. The remainder of the pile showed little evidence of oxidation.

The pile had several distinct drainage areas. Instruments were set up to measure the flow rate and water quality from each of these areas. There were also a number of springs around the base whose flow rates were measured. These springs were fed by some sort of internal storage pool in the pile. Test wells in the pile confirmed the existence of such a pool, but did not define its exact nature. This pool was recharged by precipitation and supplied a significant flow rate between storms. Depending on the section of the pile, 40 to 75 per cent of the precipitation was recovered as surface runoff. The runoff was analyzed for sulfate and acidity. Generally, these were at a maximum concentration at the beginning of the storm, and tailed off as the acidic products were removed.

Since the runoff data had some scatter, Good developed a 0.1-acre irrigation sprinkler plot. Precipitation could be simulated by sprinkling uncontaminated water on the plot at any desired rate. Again, the drainage was measured and analyzed. Based on all data, Good estimated that about 30 per cent of the water from a given storm entered the pile and later emerged via springs. The daily acid production was estimated as 200 lb/acre.

Brown[5] studied the transport of oxygen through layers of soil and material from coal refuse piles. He attempted to model the transport, but he encountered difficulty in estimating the diffusivity of air through the soil. Brown obtained laboratory scale oxidation rates for material from the Truax-Traer pile Good had studied. The small-scale rates checked closely with those obtained by Good.

The projects discussed in this section have been oriented toward developing information about natural pyrite systems. The results have been in accord with the reaction kinetics developed in laboratory investigations. Although Smith and Shumate[37] and Good[13] furnished data on acid removal rates, no removal mechanisms were suggested and evaluated. This subject of removal mechanisms and rates is one of the areas where information and theories will be developed as the model is constructed.

SECTION V

EXPERIMENTAL PROGRAM

While much experimental information is available on oxidation rates, no work has been done to determine removal rates. To counteract this deficiency, several relatively simple experiments have been performed.

ACID REMOVAL FROM ISOLATED COAL BLOCKS

Blocks of coal were isolated from the main seam in Auger Hole No. 2B at the McDaniels Research Site. One-foot square blocks were isolated by cutting channels 6 to 12 inches deep around the blocks, and then filling the channels with polyurethane foam. The foam provides a barrier to oxygen and water vapor. The block is exposed to the atmosphere only on the front face and only to other coal on the rear face. At the time of the foaming, Plexiglas® drainage trougns were placed in the horizontal channels.

Periodically, at 4 to 8 week intervals, the faces of the blocks have been washed. One liter of water was placed in a polyethylene squeeze bottle and the block was sprayed. The wash water was collected and returned to the laboratory for analysis. About 65 to 75 per cent of the water was recovered; the remainder was lost by splashing. The recovered water was assumed to be the average composition, and all calculations have been based on one liter of wash water.

The wash water was analyzed for acidity by hot titration to the phenolphthalein endpoint, and for sulfate by barium sulfate precipitation. The wash water was acidified, and atomic adsorption spectrophotometry was used to determine the iron concentration.

The acidity and sulfate are virtually identical since the wash water contained no alkalinity. The acid removal rates for a block are shown in Fig. 1 as a function of time. After an initial peak at the beginning of the test in March, 1970, the rate fell off through the summer. In October, the rate began to rise and reached a peak in January, 1971. This seasonal variation corresponds to the variation observed by Smith and Shumate[37] in the drainage from the auger holes at the McDaniels Research Site. This similarity indicates that large-scale acid removal rates can be explained by micro-scale rate variations as in the case of oxidation rate calculations. A detailed explanation of removal mechanisms and rates will be presented in Section VI.

REMOVAL RATES IN HIGH HUMIDITY CHAMBER

During the cutting of channels in the above experiment, several large blocks of coal were dislodged. Two blocks, about 1 x 2 x 4 inches in size, were placed in the bottom of a desiccator. Water, instead of drying agent, was placed in the bottom of the desiccator. With the

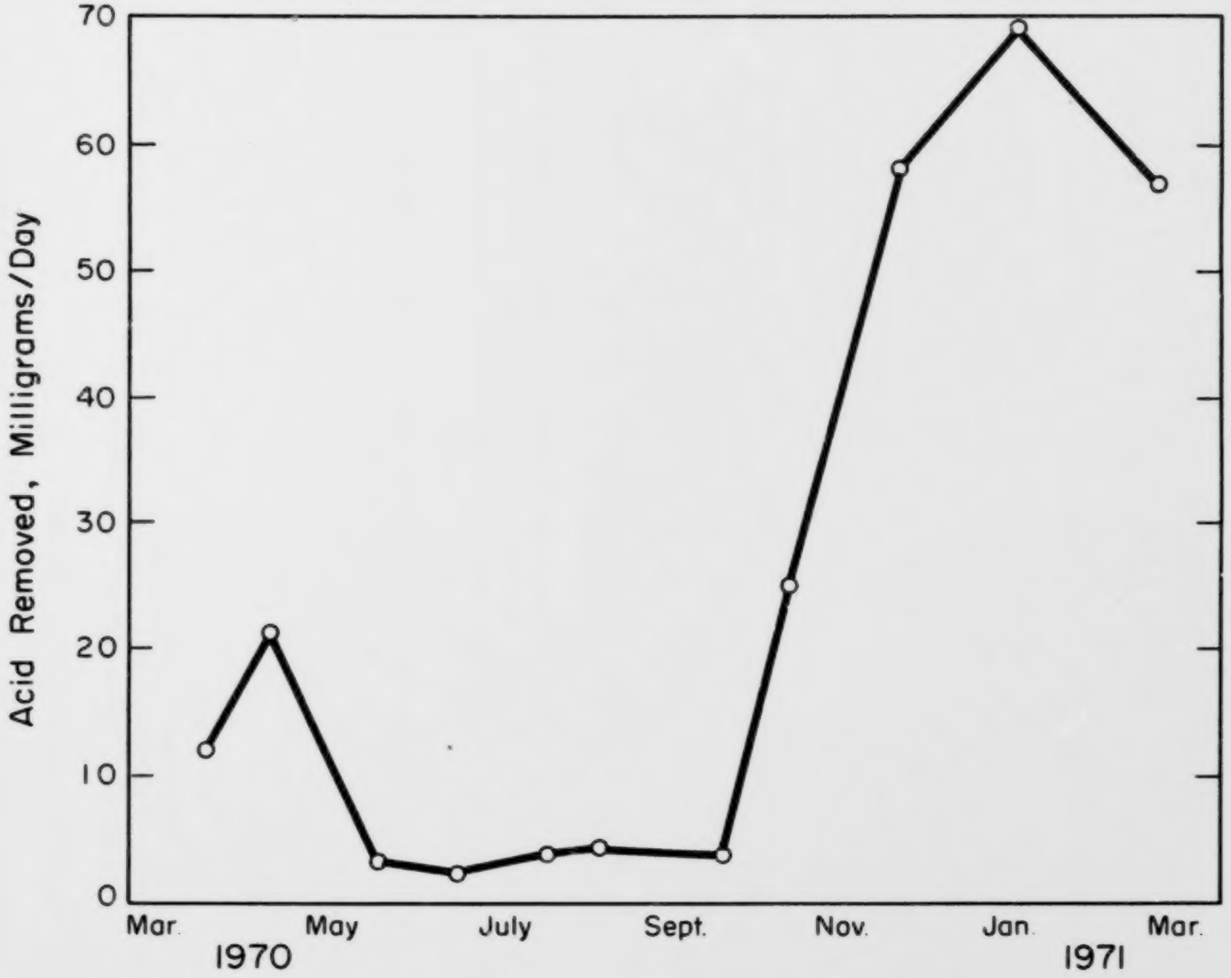

Figure 1 - Rate of Acid Removal from Isolated Coal Block

normal good seal of the desiccator, 100 per cent relative humidity was maintained in the chamber. Periodically, the lid was removed to renew the oxygen supply.

Although the blocks were sitting above the water, they gradually became wet, and occasionally drops of water would fall back into the main body of water. This experiment was continued for several months. At the conclusion of the run, the bottoms of the blocks were rinsed with distilled water. This water was added to the water in the chamber and analyzed in the normal manner for acidity, sulfate, and ferrous and ferric iron.

During the first test of 196 days, the acid removal rate for both blocks was 14.4 mg/day, the sulfate removal was 2.4 mg/day, and the iron rate was 3.3 mg/day. The ferric-ferrous ratio was 1.6. When the test was repeated for a 72-day period, the acid removal rate was 5.5 mg/day and the sulfate rate was 4.2. The iron rate increased to 13.1 mg/day, while the ferric-ferrous ratio was only 0.24. These two sets of data have much scatter, but they do give an order of magnitude estimate of the rate of the gravity diffusion type of removal mechanism which will be presented in Section VI.

The weight of each blocks was about 200 grams. When a removal rate per day per gram of coal is calculated, values are in the range of 1 to 10 μg/day. It is interesting to observe that Larez'[18] estimates of oxygen uptake by coal and shale samples fell in this same range. This agreement is particularly significant since there has been very little other experimentation with naturally occurring materials regarding oxidation and product removal rates.

SULFATE AND ACIDITY ANALYSES

In their work with acid mine drainage in Indiana, Agnew and Corbett[1] raised questions about methods of analyzing drainage. In particular, they observed that calcium and magnesium hardness ($CaCO_3$ and $MgCO_3$) should be considered in drainage analyses. Their results showed that the sum of acidity plus hardness, in consistent units, was equal to the sulfate.

To check this observation, samples from McDaniels Mine and the six auger hole mines at the McDaniels Research Site were taken in the usual manner. A small portion of the sample was acidified to prevent precipitation. The usual sulfate and acidity analyses were run on the bulk sample. Atomic absorption spectrophotometry was used to determine calcium and magnesium in the acidified samples. The acidity, sulfate, and calcium and magnesium data are tabulated in Table 1. The concentration of each has been converted to an equivalent calcium carbonate basis as is usually done for the acidity determination. The sum of acidity and hardness are in excellent agreement with the sulfate values in all cases. These results are in accord with the observations of Agnew and Corbett.[1]

TABLE 1

DRAINAGE ANALYSES DATA

Source (Date)	Metal Ions (ppm)		$CaCO_3$ Equivalent (ppm)		Acidity (ppm) $CaCO_3$	Total $CaCO_3$ Equivalents (ppm)	Sulfate (ppm)
	Ca	Mg	Ca	Mg			
McDaniels Mine (12-15-69)	15	10	36	40	72	148	133
McDaniels Mine (8-6-70)	16	9	38	35	87	160	154
Auger Hole No. 1 (8-12-70)	70	22	168	87	265	520	533
Auger Hole No. 2A (8-12-70)	118	57	290	225	1665	2180	2108
Auger Hole No. 2B (8-12-70)	25	11	60	43	60	163	169
Auger Hole No. 3 (8-12-70)	107	23	126	91	270	487	491
Auger Hole No. 4 (8-12-70)	90	27	216	106	152	474	453
Auger Hole No. 5 (8-6-70)	81	22	194	87	225	506	525
Auger Hole No. 6 (8-6-70)	111	35	266	138	347	751	757

COMMENTS

These relatively simple and crude experiments have provided information about the rate of product removal from a small volume of coal. These data, along with all of the oxidation information, will be used in the development of a model of a pyritic system in the following sections.

The calculations involving water hardness have shown that the alkalinity of the receiving waters must be considered in our model.

SECTION VI

THEORETICAL BASES OF A PYRITIC SYSTEM MODEL

"Iron pyrite reacts in the presence of oxygen and water to form iron sulfate and sulfuric acid. These products are removed and frequently have deleterious effects on the receiving body of water." The preceding phrases are a verbal model of acid mine drainage. A mathematical model of acid mine drainage starts with the verbal model and precisely quantifies and computationally defines each event in the verbal model.

The items to be quantified include how much oxygen reacts with how much pyrite at what rate in the presence of how much water? Additional questions include in what manner and how fast do the acidic products get to the receiving waters? These factors as well as others suggested by the previously discussed research investigations will be evaluated in the following sections.

There are different kinds of pyritic systems such as drift mines, auger holes, deep mines, and refuse piles. A single model capable of describing all of these systems would be cumbersome and difficult to use. Therefore, a model will be developed to describe one particular system. Suggestions and techniques for generalizing the model to fit other systems will then be offered.

A drift mine was selected for the initial model. This system was chosen because Smith and Shumate[37] have obtained detailed and fundamental information about a drift mine, and McDaniels Test Mine can furnish a check on the validity of the model. In addition, the auger holes at the McDaniels Research Site provide an opportunity to test the generality of the initial model.

An acid mine drainage system has two major subsystems; i.e., (1) pyrite oxidation, and (2) oxidation product removal. Each of these areas will be discussed separately. The oxidation presentation, based on experimental and theoretical information, is applicable to all pyritic systems. The removal section is based on general knowledge, but has less experimental data to support the presentation than does the oxidation discussion.

DERIVATION OF OXYGEN CONCENTRATION GRADIENT

The reaction mechanism and the kinetics of the oxidation of concentrated pyritic material have been described in the review of previous laboratory work. Certain conclusions will be reiterated to aid in the development of the oxidation model.

One observation was that the oxidation rate was proportional to the oxygen concentration. In the mine environment it is possible to measure a bulk oxygen concentration in the main cavity. However, this

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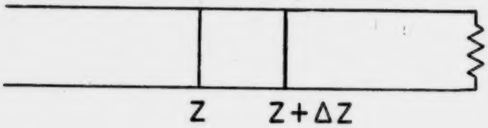
concentration is only applicable to oxidation occurring on exposed coal surfaces. Since oxidation products have been observed along cleavage planes within coal away from an exposed face, oxidation obviously occurs well back in the hill. Therefore, some method of estimating oxygen concentration within the pyrite-containing material must be developed. Since no direct analyses are readily available, a mathematical analysis will be used.

The analysis begins by assuming that oxidation occurs along the walls of small channels in the coal or shale. The channel has cross sectional area, A, and extends distance, L, into the binder. Reaction occurs the length of the channel at a rate proportional to the oxygen concentration C_{Ox}. The rate may also be assumed so slow that no oxygen gradient exists across the area A.

Consider an element in the channel of ΔZ length as shown in the sketch below.



The oxygen entering this volume at Z is $AN_{Ox_Z}\,\Delta\theta$, where N_{Ox} is pound moles per hour per square foot and $\Delta\theta$ is the time increment in hours. The oxygen leaving the volume at $Z + \Delta Z$ is $AN_{Ox_{Z+\Delta Z}}\Delta\theta$. The oxygen consumed by reaction is $k_R C_{Ox} A\Delta Z\Delta\theta$, where k_R is the reaction rate constant with units of reciprocal hours and C_{Ox} is the oxygen concentration in pound moles per cubic foot of gas. The accumulation of oxygen in the volume is $\Delta C_{Ox} A\Delta Z$. These terms can be collected in the following form: input minus output equals reaction plus accumulation, or

$$AN_{Ox_Z}\Delta\theta - N_{Ox_{Z+\Delta Z}}\Delta\theta = \Delta C_{Ox} A\Delta Z + k_R C_{Ox} A\Delta Z\Delta\theta$$

If all terms are divided by $A\Delta Z\Delta\theta$, and the limits are taken as the differential elements approach zero, the following equation is obtained:

$$\frac{\partial N_{Ox}}{\partial Z} - k_R C_{Ox} = \frac{\partial C_{Ox}}{\partial\theta}. \qquad (1)$$

The oxygen concentration term, C_{Ox}, can be replaced by $X_{Ox}C$, where C is the total gas concentration in pound moles per cubic foot and X_{Ox} is the mole fraction of oxygen in the gas. This substitution yields the general equation

$$\frac{\partial N_{Ox}}{\partial Z} - k_R X_{Ox} C = \frac{\partial C_{Ox}}{\partial \theta} . \tag{2}$$

Equation (2) is a general relationship which can only be solved by making specific assumptions and substitutions for given situations. For this analysis, it is reasonable to assume that there is no time dependence; an assumption that will be verified in the course of the analysis. A second condition for the solution is that an "effective" diffusivity, D, which is independent of position and concentration, be defined such that

$$N_{Ox} = -CD \frac{\partial X_{Ox}}{\partial Z} . \tag{3}$$

This condition is based on the fact that coal and shale contain voids and channels which are neither straight nor uniform. Because of the nonuniformity of the diffusion path, the normal distinctions of diffusion area, path length, and counter-diffusion become blurred. Bird, Stewart, and Lightfoot[3] have discussed the concept of effective diffusivity in detail. They presented a similar situation of the first-order consumption of a gas inside porous catalyst pellets.

When the two modifications are applied to Eq. (2) and derivatives taken, the following equation is obtained:

$$CD \frac{d^2 X_{Ox}}{dZ^2} = k_R X_{Ox} C . \tag{4}$$

This may be rearranged easily to give

$$\frac{d^2 X_{Ox}}{dZ^2} - \frac{k_R X_{Ox}}{D} = 0 . \tag{5}$$

The general solution to Eq. (5) is:

$$X_{Ox} = A \exp((k_R/D)^{1/2} Z) + B \exp(-(k_R/D)^{1/2} Z) . \tag{6}$$

The integration constants may be evaluated by use of the two boundary conditions (BC); i.e.,

$$\text{BC 1: At } Z = L, \quad X_{Ox} = 0.0$$

and

$$\text{BC 2: At } Z = 0, \quad X_{Ox} = X_{Ox_0} .$$

From BC 1, it is apparent that A is zero. Then, using BC 2,

$$X_{Ox_0} = B \exp[-(0)] = B$$

or

$$X_{Ox} = X_{Ox_0} \exp\,[-(k_R/D)^{1/2}Z]. \qquad (7)$$

In the evaluation of the oxygen gradient, some value must be assigned to the effective diffusivity. Workers in soil mechanics (see Brown[5]) have suggested using $D = 0.6\ D_{AB}$, where D_{AB} is the normal oxygen in air diffusivity.

Another solution to Eq. (2) may be developed by assuming that the atmospheric pressure varies at the mouth of the channel. If the ambient pressure increases, air containing 21 per cent oxygen will be pushed into the pore. If the outside pressure decreases, part of the air in the confined volume will be pulled out. This is now an unsteady state problem which is more easily handled by numerical than by analytical solution techniques. One simplifying assumption is that the pressure alternately increases and decreases uniformly with time; i.e., a "sawtooth" function. As in the previous analytical development, the effective diffusivity will be used to describe other motion of the oxygen molecules. These assumptions give for the oxygen movement:

$$N_{Ox} = -DC\,\frac{\partial X_{Ox}}{\partial Z} + X_{Ox}(N_{Ox} + N_N). \qquad (8)$$

The first term on the right hand side of the equation is the molecular diffusion of oxygen into the channel, and the second term is the bulk flow of oxygen and nitrogen being pushed and pulled by the pressure variations.

At atmospheric pressure the moles (Δn) of an "Ideal" gas entering the channel mouth are equal to $V/RT\Delta P(\theta)$, where V is the channel volume, R is the gas constant, T is the ambient temperature, and $\Delta P(\theta)$ is the change in atmospheric pressure as a function of time. When V is replaced by A·L and the entire equation divided by area to convert to a flux, we obtain

$$\frac{\Delta n}{A} = (N_{Ox} + N_N) = \frac{AL\Delta P(\theta)}{ART}$$

$$= \frac{L\Delta P(\theta)}{RT}. \qquad (9)$$

Finally it may be assumed that effects of gas entering (or leaving) the channel are uniformly reflected over the length of the channel;

i.e., each incremental volume gains an additional 1/V moles of gas. This in terms of the flux is

$$(N_{Ox} + N_N)_Z = \frac{L\Delta P(\theta)}{RT} (1 - Z/L) \quad (10)$$

and

$$(N_{Ox} + N_N)_Z = \frac{\Delta P(\theta)}{RT} (L - Z). \quad (11)$$

Equation (11) may be substituted into Eq. (8) and the derivative taken:

$$\frac{\partial N_{Ox}}{\partial Z} = -CD \frac{\partial^2 X_{Ox}}{\partial Z^2} + \frac{\Delta P(\theta)}{RT} (L-Z) \frac{\partial X_{Ox}}{\partial Z} - X_{Ox} \frac{\Delta P(\theta)}{RT} \quad (12)$$

Equation (12) is substituted into Eq. (2) to give the second-order unsteady state equation

$$C \frac{\partial X_{Ox}}{\partial \theta} = CD \frac{\partial^2 X_{Ox}}{\partial Z^2} - \frac{\Delta P(\theta)}{RT} (L-Z) \frac{\partial X_{Ox}}{\partial Z} + X_{Ox} \frac{\Delta P(\theta)}{RT} - k_R X_{Ox} C. \quad (13)$$

Three boundary conditions are required for the solution of Eq. (13). Two are the same distance and mole fraction parameters as used in the analytical solution. The third is a time and mole fraction parameter describing the oxygen gradient at zero time.

BC 1: At $Z = L$, $\theta = \theta$; $X_{Ox} = 0$

BC 2: At $Z = 0$, $\theta = \theta$; $X_{Ox} = X_{Ox}$

BC 3: At $Z = Z$, $\theta = 0$; $X_{Ox} = X_{Ox_0} \exp(-(k\ /D)^{1/2} Z)$

Equation (13) is of such complexity that there are no straightforward analytical solutions. However, numerical techniques using a digital computer can be used to generate solutions for different values of the independent variables L and $\Delta P(\theta)$. Implicit finite differences are used to estimate all derivatives, and a solution is obtained by iterative techniques. The setup of the numerical solution and the computer program "GRADIENT" are shown in Appendix A.

The output of the program "GRADIENT" is sets of oxygen gradients for given L and $\Delta P(\theta)$ values. An integrating function in the program estimates the daily oxygen consumption in the channel at the stated conditions. Since "GRADIENT" generates much data rapidly, the most important information will be summarized in Figs. 2 - 7.

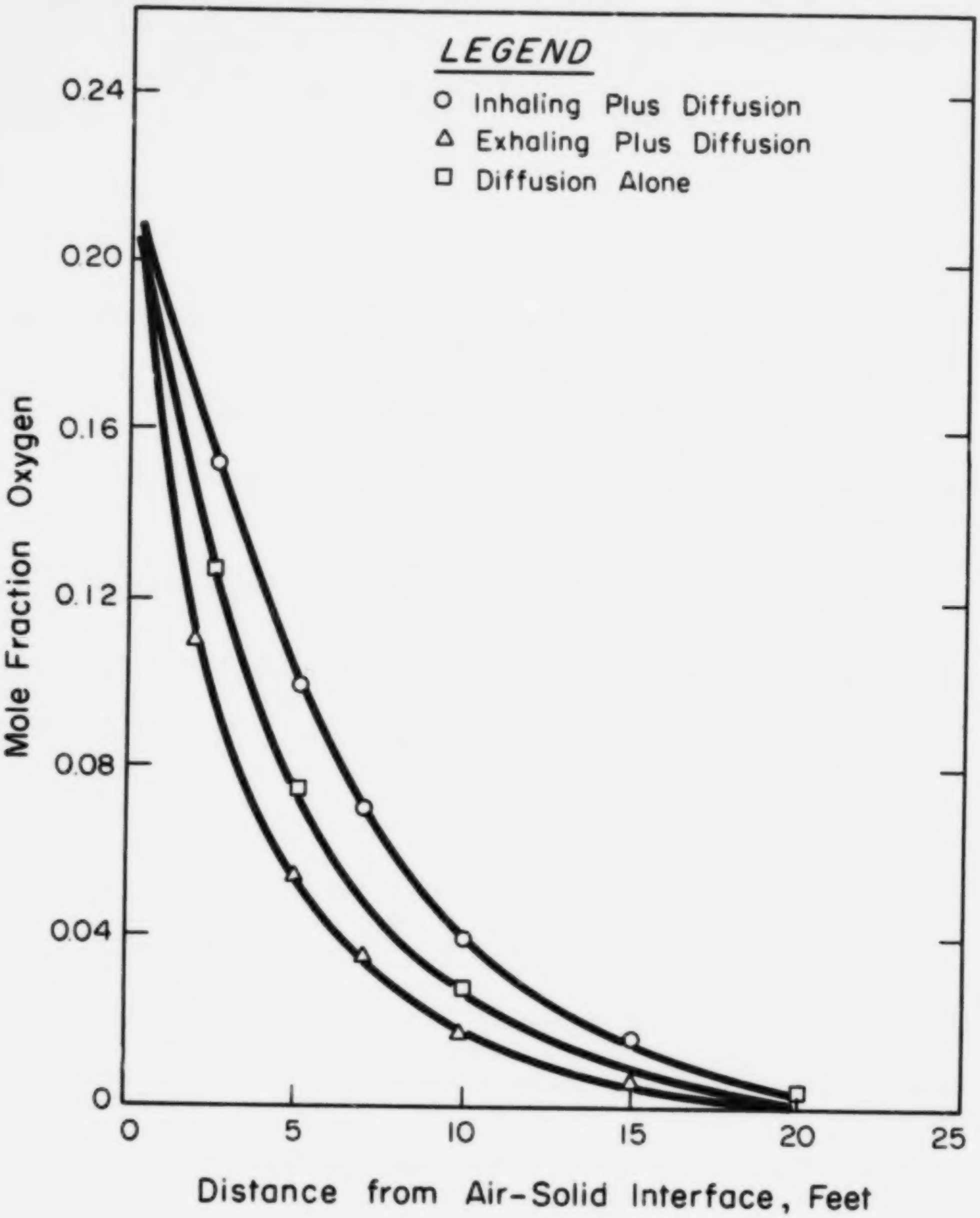


Figure 2 - Effect of "Breathing" on Oxygen Gradient

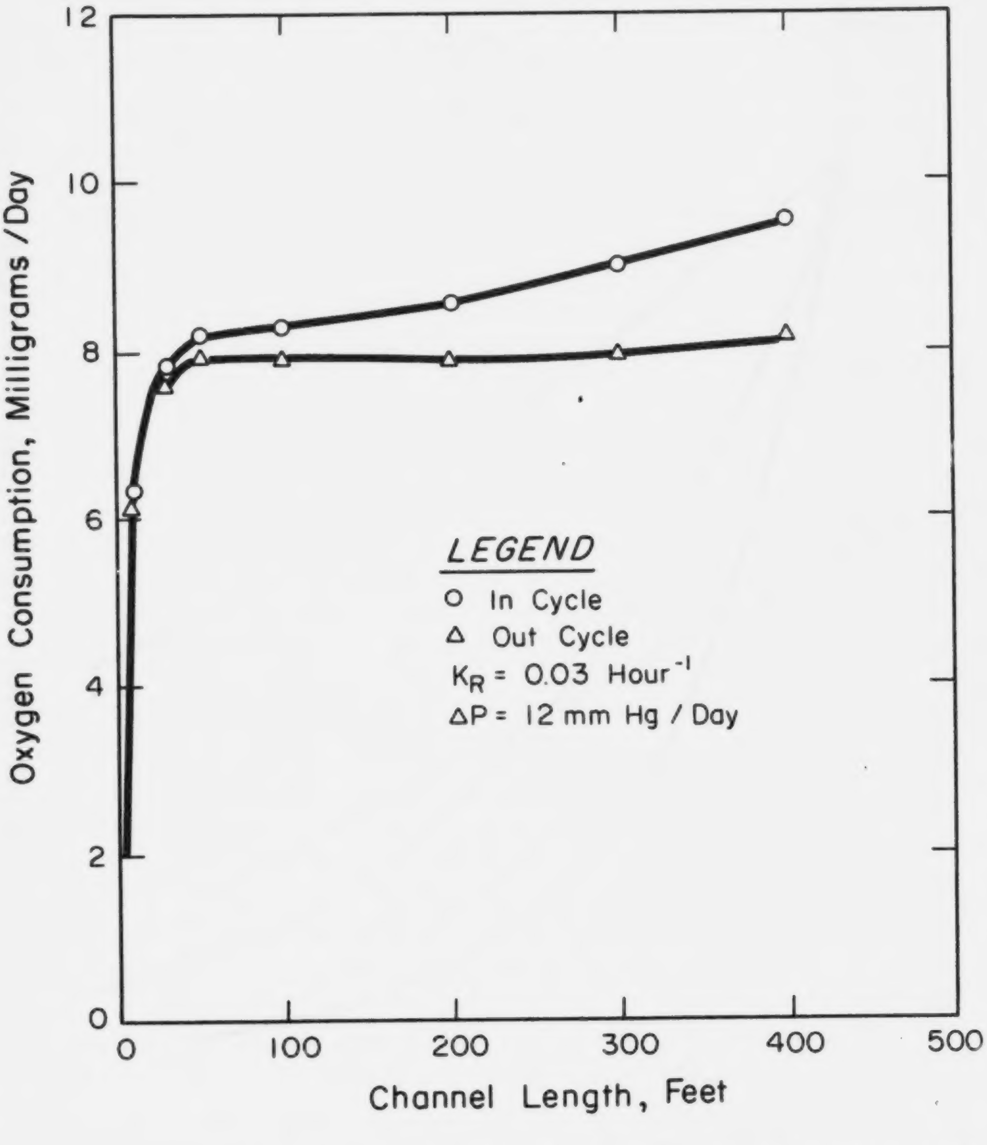


Figure 3 - Effect of "Breathing" on First Order Oxidation Rate

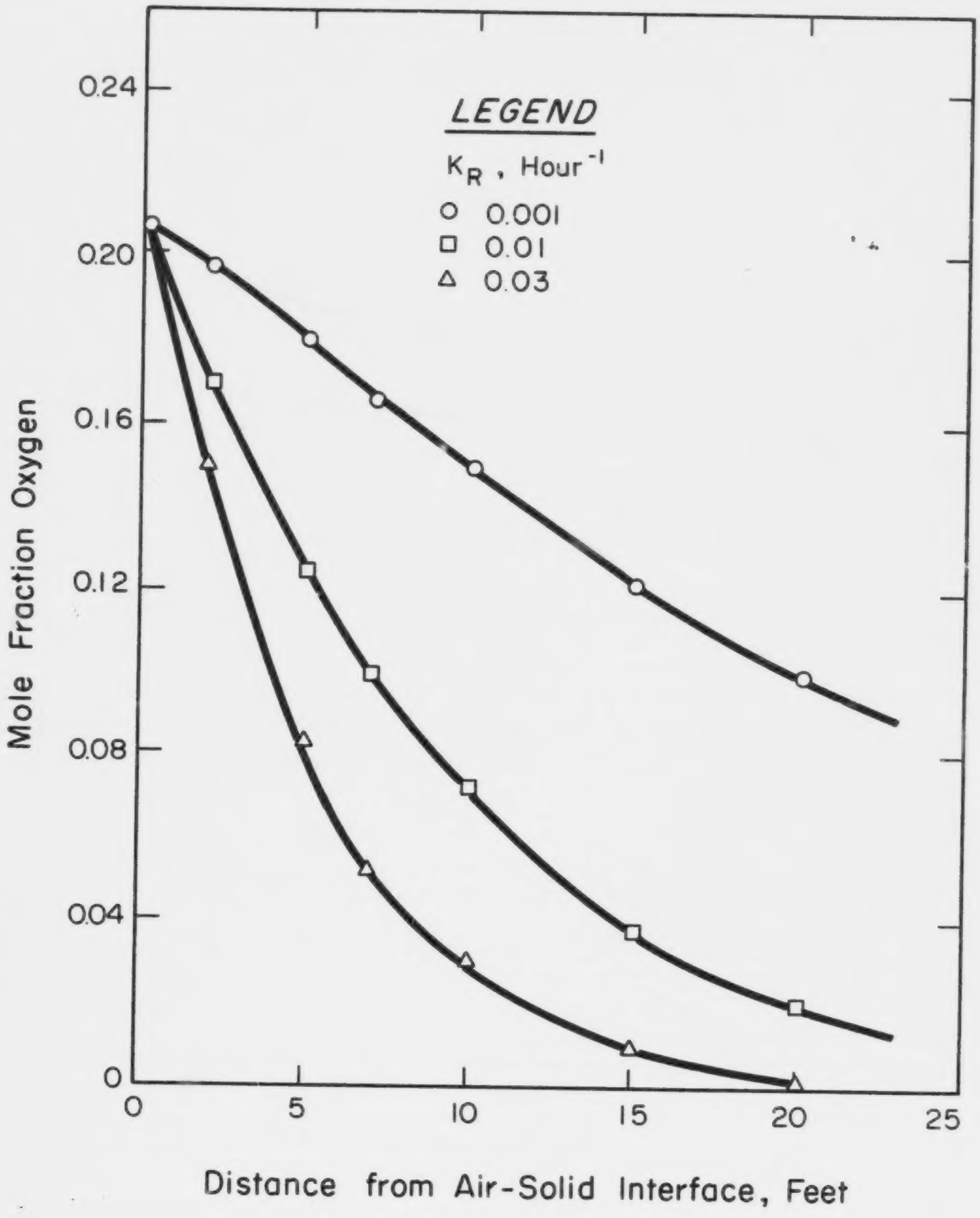


Figure 4 - Effect of First Order Rate Constant on Oxygen Gradient

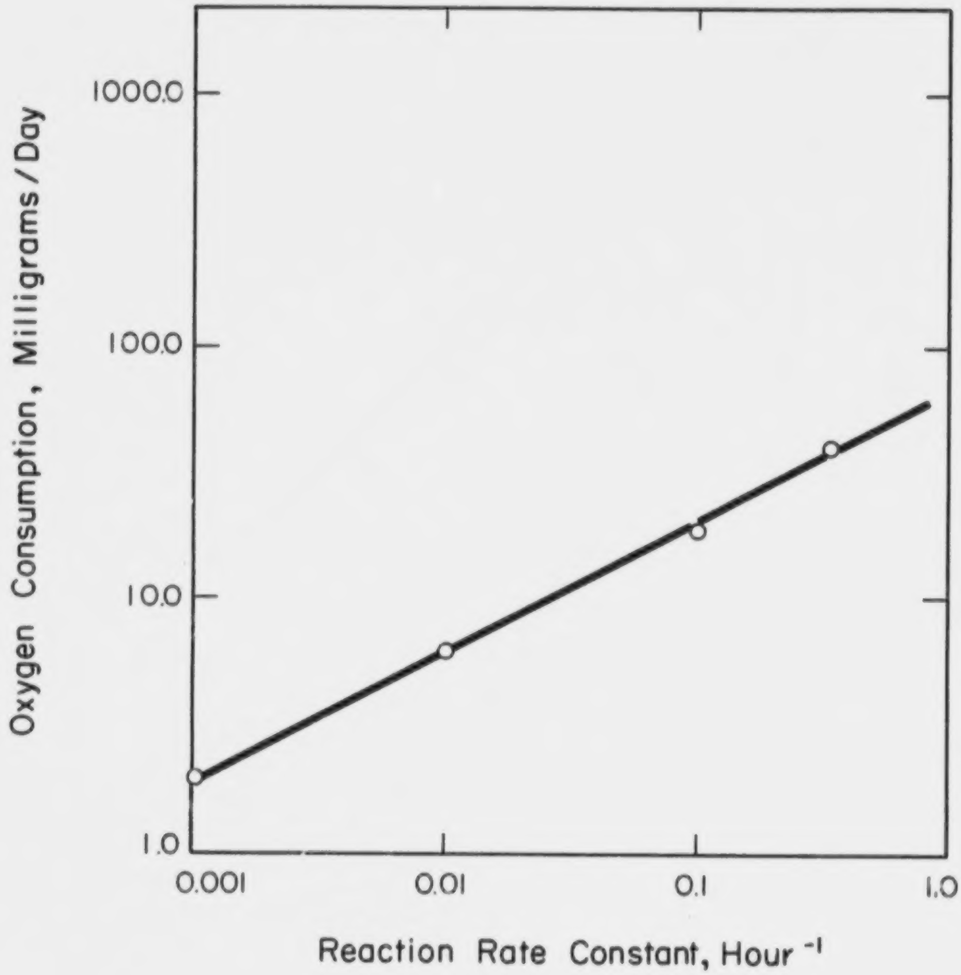


Figure 5 - Effect of Rate Constant on First Order Oxidation Rate

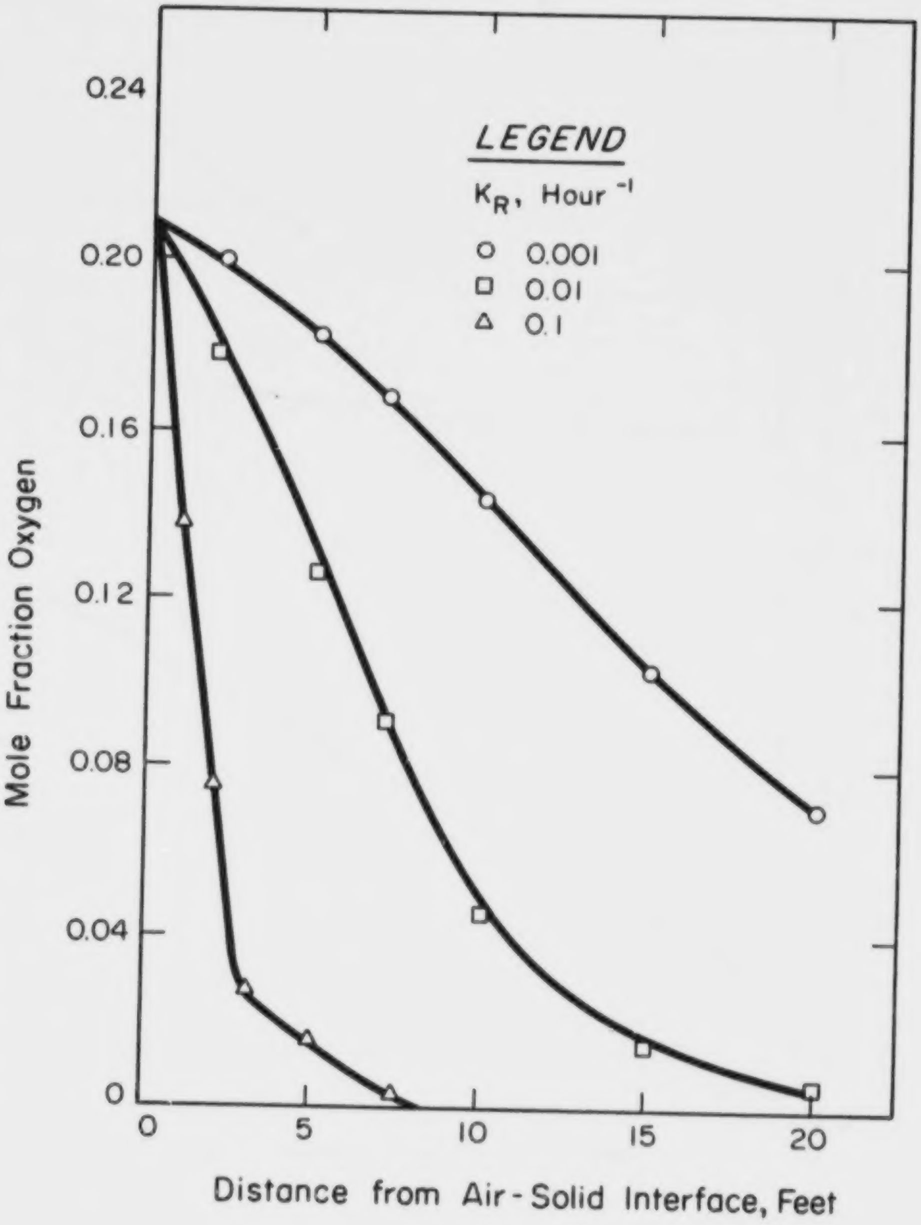


Figure 6 - Effect of Zero Order Rate Constant on Oxygen Gradient

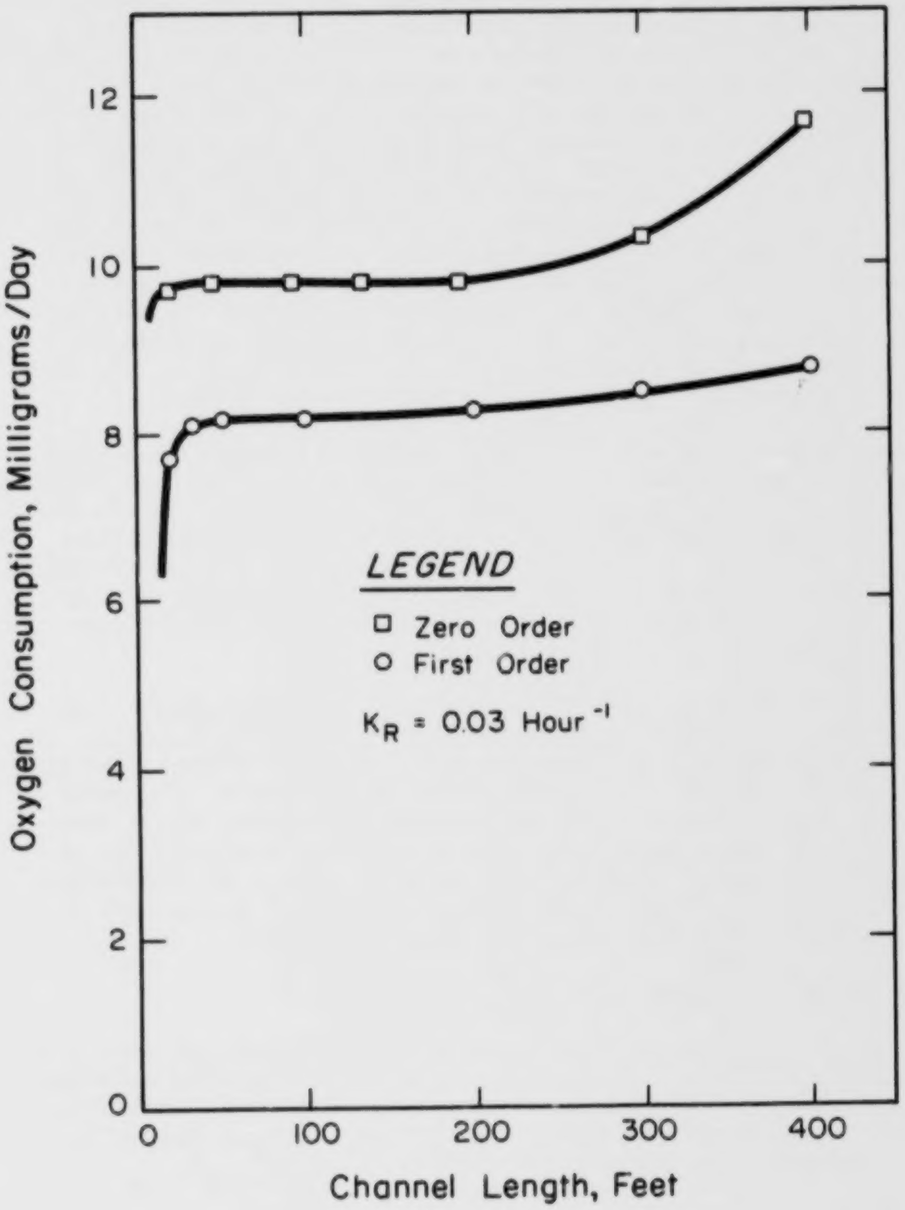


Figure 7 - Effect of Pore Length on Oxidation Rate

The $\Delta P(\theta)$ function was treated as a sawtooth variable that linearly moves between some maximum and minimum value. The maximum has been fixed at 745 mm Hg pressure and the minimum is established by the ΔP. Figure 2 shows the maximum and minimum oxygen gradients for a daily pressure change of 12 mm Hg and an L of 200 feet. At the minimum pressure, the channel has been partially evacuated, and the oxygen gradient is at its lowest level, since the highest oxygen content air has been pulled out. At the maximum, relatively oxygen-rich (21 per cent), atmospheric air has been forced into the channel to raise the gradient. For comparison, the gradient from the analytical solution (no breathing) is also shown. The analytical gradient is slightly closer to the minimum than to the maximum. Calculations for more normal, 1 to 3 mm Hg, daily pressure changes give maximum and minimum gradients closer together. At these low pressure variations, the time average of the gradients approaches the analytical gradient.

The channel length, L, is representative of the volume of gas available for compression and expansion rather than being a perpendicular distance from the channel mouth. Figure 3 shows the influence of L on the amount of oxygen consumed in the channel. As expected, more oxygen is consumed on the "in" than on the "out" breathing cycles. Longer channels increase the oxidation on the "in" steps, but give less oxidation on the "out" cycles. The net result is a slight increase of oxidation with increasing L.

The evidence presented in Figs. 2 and 3 leads to the conclusion that "breathing" has little effect on oxidation in closed-end channels. If channels between the atmosphere and a very large void volume, such as a mined out volume, were considered, "breathing" might be of greater importance. This is indicated by the rapidly increasing oxygen consumption at longer pore lengths in Fig. 3. In such a case nearly all of the pyrite-containing channel would be swept with a new atmosphere during each pressure change. However, in the current development, it seems reasonable to use the analytical oxygen gradient.

INFLUENCE OF REACTION RATE CONSTANT

The rate constant k_R also influences the oxygen gradients and amount of oxidation. Generally k_R is defined in terms of the reacting materials. In the case of a heterogeneous reaction a very careful definition is required. The reaction rate equation is written below in the usual symbolic language for a first-order reaction:

$$-\frac{dC_{Ox}}{d\theta} = k_R C_{Ox} \qquad (14)$$

The derivative, $dC_{Ox}/d\theta$, is the change in moles per unit volume per unit time. The rate constant, k_R, has the units of reciprocal time, and C_{Ox}, the gas concentration, has the units of moles per unit volume.

pyrite is embedded in the channel walls in small quantities so the actual concentration must be considered in determining k_R. Since the true pyrite distribution is not known, it is necessary to assume a distribution. For example, in the laboratory, one gram of 60-mesh, concentrated, pyritic material consumed 25 µg O_2/hr in air at 25°C. The gram of pyrite can be assumed to be distributed along the walls of some volume, V, of channel, or,

$$\frac{\text{Rate}}{\text{gram pyrite}} \times \frac{\text{gram pyrite}}{\text{Volume}} = k_R \frac{\text{mole oxygen}}{\text{Volume}}$$

$$\frac{25 \times 10^{-6} \text{ gram oxygen}}{\text{V hour}} = k_R \times \frac{0.21 \times 32 \text{ grams oxygen}}{22.4 \text{ liters}}$$

$$k_R = \frac{8.3 \times 10^{-4} \text{ liter}}{\text{V hour}}$$

If a channel cross sectional area of 1 mm^2 is considered, it is likely that the reactivity equivalent of 1 g of crushed pyrite would be found in a length of 100 m. This would give a volume of 0.01 m^3, or a k_R value of 0.083 per hour. Since this can only be considered an educated guess, Fig. 4 has been drawn to show the effect of the rate constant on oxygen gradients. The higher the rate constant, the more rapidly the gradient drops to zero. The influence of rate constant on the amount of oxidation is shown in Fig. 5 as a logarithmic plot. This plot has a slope of 0.5, indicating that the rate is proportional to the square root of the rate constant. This is the result for any rate calculation using a concentration term based on Eq. (7). The preceding observation leads to the conclusion that for a reasonably accurate oxidation model, the rate constant should be known within an order of magnitude.

EFFECTS OF REACTION ORDER

All of the discussion to this point has been based on the premise of first-order, or oxygen concentration dependent, reaction kinetics. However, in microbiological work, particularly that of Lau *et al.*,[12], it has been observed that above a certain minimum concentration of oxygen, the oxidation of pyrite is independent of the oxygen concentration. The oxidation rate appears to be some function of the *Ferrobacillus* concentration, or zero-order with respect to oxygen.

The "GRADIENT" program was modified to do zero-order calculations of oxidation above a minimum oxygen level and first-order below that level. Based on the work of Lau *et al.*, two per cent oxygen was used as the cut-off point. The oxidation rate above two per cent oxygen was considered to be the same as the rate observed at normal (21 per cent) atmospheric oxygen level.

The results generated using these assumptions lead to the same conclusions as the first-order case. Some differences in form do exist. For example, the zero-order oxygen concentration gradients shown in Fig. 6 are steeper than the first-order curves in Fig. 4. The most important difference between the two orders is shown in Fig. 7, where the amounts of oxidation are plotted against pore length for the different orders. The zero-order reaction gives a consistently higher level of oxidation than does the first-order. This occurs because the zero-order concentration gradient, the driving force for diffusion, is steeper as more oxygen enters the channel to be used in oxidation.

The difference between zero- and first-order rates is not important in the development of a model for three reasons. As a practical matter, the 30 per cent difference is minor compared to some of the other influences such as rate constants. More importantly, Smith[35] and others have stated that the significant bacterial activity, ferrous to ferric oxidation, occurs in the drainage rather than on the surface of the oxidizing pyrite. This means that in a natural system the pyrite is oxidized, the products move to a receiving stream or pool, and then the bacteria oxidize ferrous ions to the ferric state. In the laboratory research, the bacterial enhancement of oxidation rates was observed only in systems where the culture medium was recirculated over the pyritic material. In a natural system recirculation does not occur. Finally, in a natural system, the water-to-pyrite ratio is low at the reaction sites. Under this condition, as explained by Lau et al.,[19], there will be relatively few bacteria growing, and therefore, no enhancement of the oxidation rate.

OXIDATION PRODUCT REMOVAL

Generally speaking, the removal of pyrite oxidation products has been investigated much less than oxidation of pyrite. The basic removal problem is to describe and evaluate the flow rate of oxidation products through various porous media by both water movement and by molecular diffusion in aqueous solution (i.e., without net flow of water).

The rate of removal is primarily a function of the hydrologic characteristics of the system. Conditions describing the extremes of removal rate compared to oxidation rate can be imagined as varying from oxidation sites in close proximity to flowing ground water to sites far removed from the water table which are never inundated or flushed by blowing water. All other factors being equal, oxidation rates at these sites would be the same, but the rate of acid transport to the effluent stream would be quite different. To estimate the rate of transport, we must first describe possible transport mechanisms.

Removal Mechanisms

On the basis of laboratory observations and physical considerations, it is possible to visualize three parallel transport mechanisms.

The first is simply a direct washing. As ground water percolates through flow channels in the coal seam, products from the walls of the pores are dissolved. These products may have formed at times when the channel was not filled with water or the products may have diffused from adjacent channels that are not normally used for water flow. As flow increases, more channels are utilized, and more product is removed.

The second removal mechanism is the flushing of products from an inundated volume. The inundation occurs as the water table rises during the spring thaws or during heavy rains and covers a previously nonsaturated volume. The oxidation products gradually dissolve and are carried to the receiving stream. This mechanism is partially responsible for the high acid loads observed during the spring.

The final removal mechanism arises from the fact that the oxidation products form a highly localized concentrated acid and salt solution. This solution is hygroscopic and will absorb moisture from the air. Since the relative humidity in a mine atmosphere is usually 100 per cent, ample water is available for absorption. In addition, when warm air from outside enters a mine and is cooled, moisture may be removed by condensation. Eventually, sufficient moisture is collected at the oxidized surface, and droplets of acidic solution form. As the drops become heavier, they begin to flow by gravity and eventually reach the receiving streams. This mechanism has been observed in laboratory studies where water-saturated air was recirculated over a bed of pyritic material. After about one week, acidic brown liquid began to drip from the pyrite bed. The removal by condensation, or gravity diffusion in the nomenclature of this model, is assumed to occur uniformly throughout a pyritic system, but only the drops leaving the bottom of the system are included in the net removal of acid.

While experimental data and theoretical calculations could be used to closely estimate oxidation rates in a pyritic system, fewer data are available for estimating the rate of removal by each of the described removal mechanisms. However, using "common sense" and the engineering approach of Smith,[37] removal rates can be estimated in terms of what is physically reasonable.

Gravity diffusion both adds and removes products from a volume of coal or shale. The rate of removal by this method can be estimated in two ways. The laboratory experiment with a small coal block in a 100 per cent relative humidity chamber gave a removal rate, R_{Rem}, of about 100 μg acidity per day per square foot of coal drainage surface. If the rate of gravity diffusion is considered proportional to the quantity of oxidation products stored in a volume, the above removal rate is a maximum estimate since it represents a volume at the air-solid interface where the oxygen concentration and oxidation rate are at a maximum. If the rate of removal by gravity diffusion is assumed proportional to the concentration of stored products, the total removal rate from a one-foot wide row of volumes perpendicular to the interface may be estimated by integrating the exponential oxidation gradient of Eq. (7); i.e.,

$$\text{Total removed} = R_{\text{Rem}} \int_0^L \exp(-(k_R/D)^{1/2})dZ.$$

Inserting the value of k_R equal to 0.8 per day for coal, a diffusivity of 10.0 square feet per day, and the R_{Rem} value of 100 mg acidity per day and noting that at great values of L there are no oxidation products to be removed, then

$$\text{Total removed} = (100/(0.8/10)^{1/2})\exp(-(0.8/10)^{1/2})$$

$$= 343 \text{ mg acid per day per foot of interface.}$$

For the estimated wall length of 100 feet at McDaniels Mine this gives 34 g per day or about 2 lb per month.

The second method of estimating gravity diffusion is to examine acid output data from McDaniels Mine for periods such as late summer and early autumn when the ground is relatively dry and ground water flows are low. Under these conditions, leaching and inundation removal of oxidation products are minimal, and gravity diffusion is the dominant removal mechanism. Over the 1966 to 1970 period, acid loads in this dry season have been in the range of 2-4 lb per month at McDaniels Mine. Since this range agrees with the rate estimated in the laboratory study, a relationship must be included in the model to give this rate of removal by gravity diffusion.

The removal of products by percolation or by flushing requires that there be a description of underground water flow patterns. Hydrologic equations have been developed to describe flow patterns in watersheds covering hundreds of square miles. Even in these large areas, the nonisotropic nature of the earth forces generalizations in the flow descriptions. When the relatively small (at most two or three acres) drainage area of McDaniels Mine is considered, flow can best be described as "through cracks and crevices."[32] It has been suggested that the best mathematical description of this behavior can be obtained by assuming a model and determining how well the model correlates previous precipitation and flow data.

Soil Layer Water Balance

Assuming that the source of water for mine drainage is precipitation as rain or snow, over a hydrologic year the total drainage can be related to the precipitation over a specific watershed area. However, the degree of saturation of the soil affects water infiltration so that the rate of water passing through the ground surface to the sub-surface aquifer varies. If a water balance is made on the soil layer, the degree of saturation can be calculated and the amount of water going to storage (for drainage flow) can also be determined. The following paragraphs describe the development of the calculations.

Water balance

As a general rule in material balance, the amount of material coming into a system minus the amount going out of a system must be equal to accumulation. For water balance in the soil layer, precipitation as rain or snow is the "in"; excess infiltrated water for drainage flow (ADD), evapo-transpiration (PEVAP), and runoff (RUNOFF), if any, are the "out"; and the water stored in the soil layer or root structure (PWATER), is the "accumulation."

The equation describing the balance is

$$\mathrm{PWATER} = \mathrm{RAIN} + \mathrm{EMRNF} + \mathrm{SWMELT} - \mathrm{RUNOFF} - \mathrm{PEVAP} - \mathrm{ADD}, \qquad (15)$$

where EMRNF is the difference between excess water and RUNOFF, and SWMELT is the amount of melted snow.

During warmer weather [that is, when the mean temperature (TMEAN) is greater than 32°F] any precipitation is considered as rain. If the provisional water holding capacity (PWHC) can be determined by the method of Thornthwaite and Mather,[42] the difference between PWHC and the moisture content of the soil (PWATER) is equal to the deficiency of water in the soil (DEFICT). If the rainfall is larger than the deficiency, excess water (EXCS) will be removed as surface runoff. For our model, 92% of the excess water is assumed to run off; the rest (i.e., EMRNF = EXCS - RUNOFF) is included in the water balance as "In." When the mean temperature is less than 32°F, precipitation is considered to be snow that will stay on the ground surface until the mean temperature is higher than 32°F and the ground thaws. Wisler and Brater[44] estimated that 0.1 inch snow is melted for each degree day above freezing. The melted snow (SWMELT) is then treated the same as rainfall.

The "out" for the water balance of the soil layer includes the water going into storage for drainage flow (ADD), evapotranspiration (PEVAP), and runoff (RUNOFF), if any. The method of Thronthwaite and Mather[42] can be used to estimate PEVAP (directions on how to use this method are provided in Appendix B); however, PEVAP depends on the moisture content in the soil layer. The efficiency factor (EFF) for PEVAP is equal to the degree of saturation; i.e., the ratio of PWATER to PWHC. For example, PEVAP is equal to 2.00 for the month of April, or an average of 0.066 for each day in April. A day having 100% soil saturation will have a larger PEVAP value (0.066) than a day with a 50% moisture saturation (PEVAP = 0.033). The excess infiltrated water, ADD in Eq. (15), will leave the soil layer and go into the storage aquifer (TANK) for drainage flow.

ADD was assumed to be a function of temperature and (PWATER/PWHC) = WOVERW. For a "ballpark" estimation for the effect of WOVERW, a straight-line relationship with ADD was assumed, since the more saturated the soil, the more water will be available for entering storage. To consider the effect of temperature, a factor (FADD) was defined which varied from a low value at temperatures below 32°F to a high constant value for temperatures above 45°F. Basically, FADD is used to describe the mobility of water in the soil layer. Equations for determining FADD are given in Appendix E.

At this point, all the components in the water balance equation have been defined. The root storage water for any day can be calculated by adding the net amount of the water to the PWATER of the previous day as shown in Eq. (16).

$$\underset{\text{(new)}}{\text{PWATER}} = \underset{\text{(of previous date)}}{\text{PWATER}} + \text{RAIN} + \text{EMRNF} + \text{SWMELT} - \text{ADD} - \text{PEVAP} - \text{RUNOFF}. \quad (16)$$

The amount of ADD for any one day can then be determined and added to the aquifer storage of that day. The concept of the aquifer storage (TANK) is discussed below.

Watershed area, storage and flow

Morth[25] suggested that drainage flow (FLOW) can be calculated as a function of the storage and drainage area of the mine. Linear relationships between these variables were found by Morth to give the best results. For the purpose of finding the dependent variable, drainage flow, the independent variables, watershed area, and storage, must be determined first.

Watershed area (WSHED) is the ground surface area through which water passes to provide the drainage flow water. Knowing the drainage for a year and the annual ADD water, watershed area can be calculated. Since the auger holes and McDaniels Mine have the same soil layer and temperature conditions, McDaniels Mine should have a larger WSHED than the auger holes, since higher annual drainage flow was recorded for the mine.

The "out" of the water balance for the soil layer are PEVAP and ADD. The latter will enter the aquifer of the mine. This aquifer can be treated as storage for the drainage flow.

The concept of TANK representation for the storage of drainage flow is hypothetical. For a one-tank representation, the volume of storage water would be the height or the value of TANK times the watershed area, WSHED. In other words, the storage is a very flat rectangular box, since the ratio of TANK/WSHED is extremely small.

The volume of water stored, not the volume occupied by the water-saturated part of the aquifer, is represented by TANK times WSHED. The height of water, HEAD, which provides the driving force for FLOW, also depends on the void fraction and shape of the aquifer. The relationship between TANK and HEAD can be determined from experimental data as shown in Appendix E. If experimental data are not available, a linear relationship between TANK and HEAD may be assumed.

SECTION VII

DEVELOPMENT OF DRIFT MINE MODEL

Several approaches are possible in developing a model of a pyrite system. The major source of variations arises in the choice of the bases to be used. The choice of a coordinate system depends on factors such as computational facility, spatial visualization, and physical reality. The easiest choice is to list all possible variables with a tabulation of data and feed the mass of numbers to a computerized multiple regression analysis. This statistical approach offers computational facility, but sometimes at the sacrifice of physical reality. Since the goal of this research is to maintain physical meaning so that different sites can be compared, a statistical approach must be ruled out.

For the sake of generality and physical significance, the best approach is to work with Cartesian coordinates. The physical orientation of the system can be easily described in these coordinates. Physical and chemical variables such as water flow, oxygen gradients, and the water table are also easily defined in rectangular coordinates.

Computational neatness can be assured by the careful definition of the variables. For example, a technique to calculate the oxygen gradient in terms of the distance from the air-solid interface has already been explained.

DESCRIPTION OF MICRO-SYSTEM

Let us begin development of the computational model by examining a sketch of a pyrite-containing coal seam as shown in Fig. 8. Generally, the coal seam is divided into a number of layers of coal and shale. The water table may intercept the coal seam, which extends a relatively great distance from the air-solid interface.

One of the layers is shown in expanded form in Fig. 9. The stratum is of such size that oxidation and removal conditions can vary widely over the stratum. Therefore, the stratum is subdivided into several layers, and these layers are then divided into blocks. The basic assumption of whole model must now be stated: An average set of conditions exists over each volume and can be used in any calculations for that block. The system behavior is then the linear sum of the behavior of all these small reaction volumes.

The block marked "A" in Fig. 9 is further expanded in Fig. 10. A material balance has been developed about the block to relate the oxidation product formation and removal rates. Oxidation is the chemical reaction of oxygen and pyrite. Gravity diffusion is the very slow downward movement of highly concentrated product solutions. Leaching is the removal of products by ground water trickling through the oxidized voluem. Flooding is the removal of products when a volume is inundated.

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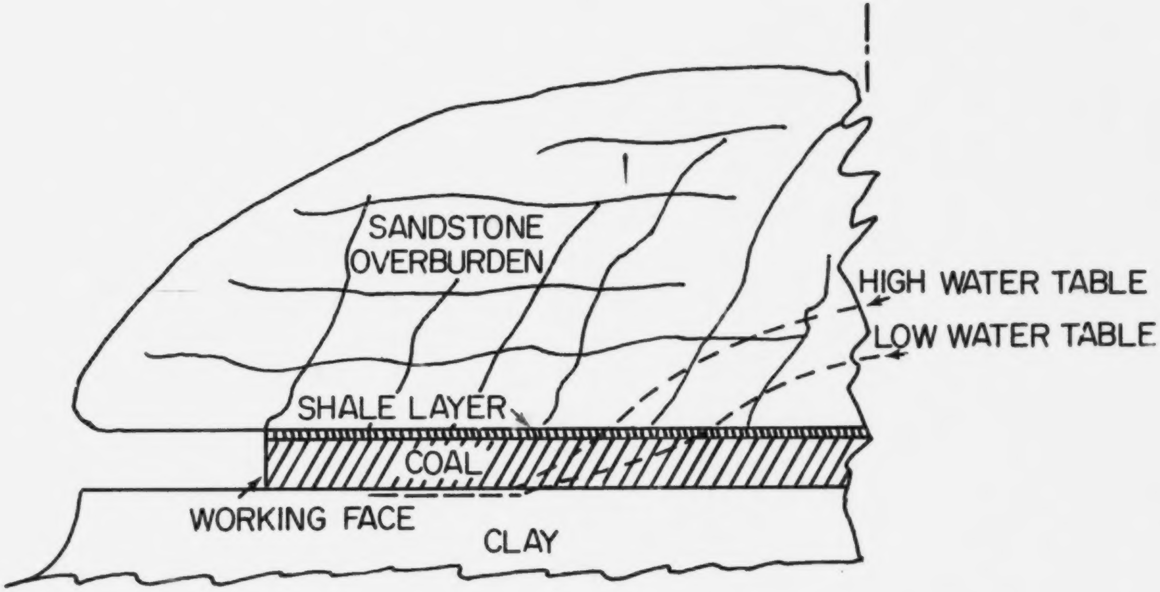
SANDSTONE OVERBURDEN
HIGH WATER TABLE
LOW WATER TABLE
SHALE LAYER
COAL
WORKING FACE
CLAY

Figure 8 - Sketch of Underground Pyrite System from Smith and Shumate (37)

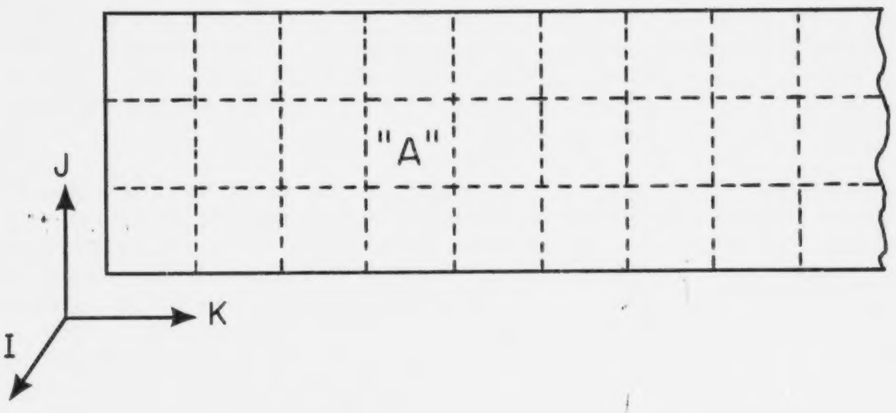

Figure 9 - Stratum in Seam Divided into Micro-Volumes

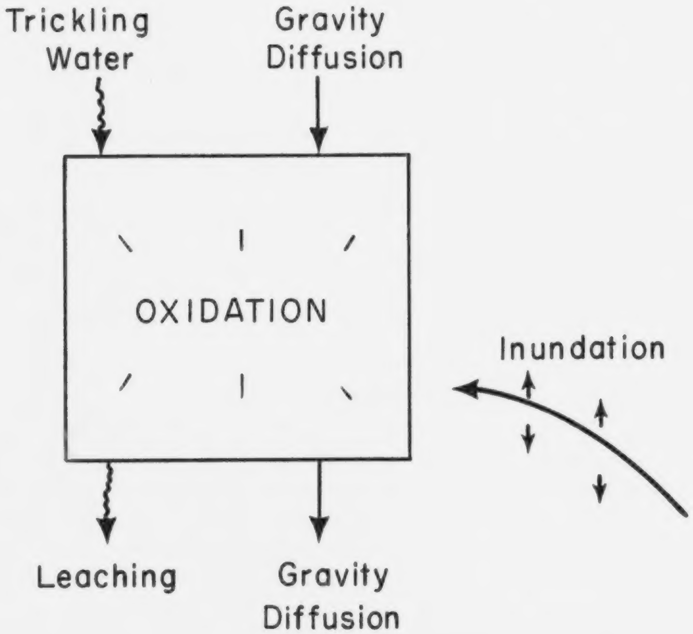
Trickling Water
Gravity Diffusion
OXIDATION
Inundation
Leaching
Gravity Diffusion

Figure 10 - Storage Volume Material Balance

All of these terms have been described so now they need only be slightly expanded or altered to give a single expression to describe the events in volume "A."

Oxidation rate is a function of the oxygen concentration, the pyrite surface available for oxidation, and the reaction rate constant. The oxygen concentration gradient can be calculated using Eq. (7). The pyrite available and the reaction rate constant can be estimated from data such as that described by Larez.[18]

Previously, a rate constant was calculated by assuming that the reactivity of a gram of pulverized pyrite was distributed along the walls of some void volume. Larez, however, reported rates based on a volume of binder material rather than on the basis of pyrite weight or surface area. In this case, the void fraction, ϵ, of the binder must be used in calculating the rate constant. For shale, ϵ is in the range 0.2 to 0.3.[35] For coal, the only data on porosity are of the micro-structure measured by nitrogen adsorption and other such techniques. Therefore, it has been necessary to make a rough estimate of ϵ for coal. Dr. K. S. Shumate, of the Civil Engineering Department of The Ohio State University, has suggested that ϵ probably has a relatively low value for coal--in the range 0.005 to 0.02.[32] For computational purposes a value of 0.005 void fraction will be used for coal.

Larez' oxygen uptake rates and the void fraction may be used to estimate a rate constant for the naturally occurring pyrite. We may write the general first-order rate equation as

$$\text{Rate(moles/hour/volume gas)} = k_R\text{(1/hour)}\ \ C_{Ox}\text{(moles oxygen/volume gas)}.$$

The experimental rate, Rate_{Exp}, was reported as oxygen uptake per total volume of solid per hour. Since the gas volume equals the void fraction times the total volume,

$$\text{Rate}_{Exp}/\epsilon = k_R \quad C_{Ox}.$$

This may be rearranged to give

$$k_R = \text{Rate}_{Exp}/(\epsilon\ C_{Ox}).$$

If an oxygen level of 21 per cent is assumed in the bulk air phase, and Larez' oxygen uptake rates of 3 $\mu g\ O_2 \cdot hr^{-1} \cdot cm^{-3}$ solid for shale and 1 $\mu g \cdot hr^{-1} \cdot cm^{-3}$ for coal are used, k_R has a value of 0.067 per day for shale and 0.80 per day for coal. The higher value for coal arises because the rate constant is inversely proportional to the void fraction.

In the following pages, a number of variables will be introduced. The model terminology is summarized in Table 2. The basic notation used

TABLE 2

NOMENCLATURE FOR THE PROGRAM

ADD	Water entering TANK from soil layer water balance
AFLAG	Parameter denoting the month being executed
AG	Identifies the month being executed
AGO	Dummy variable for AG
ALEFT	Product storage after flooding
ALK	Factor converting acid load from oxygen consumption basis to equivalent alkalinity basis
ALKALI	Ground water alkalinity (ppm)
ALT	Elevation of stratum relative to datum plant (ft)
AMONTH	Month
AOUT	Daily acid removal by leaching (lb)
CCPRFT	Constant for calculating rate constant
CONA	Constant for calculating rate constant
CONFH	Constant relating FLOW and aquifer storage (TANK)
CON5	Conversion factor for WSHED
DEFICT	Deficiency of water in root storage (inches)
DEHK	Distance in K-direction that is flooded (ft)
DI	Length of air-solid interface increments (ft)
DIF	Base gravity diffusion constant
DIFF	Gas diffusivity (ft^2/day)
DIFFG	Gravity diffusion rate constant for a layer
DK	Length of depth increments (ft)
DSLV	Fraction of stored products removed each day by leaching
DTHETA	Time increment length (days)

DVOL	Volume of each micro-block (ft^3)
EFF	Efficiency factor for evapotranspiration
EMRNF	Excess water content minus runoff (inches)
EXCS	Excess water (inches)
FADD	Temperature factor for water entering storage
FJ	Ratio of stored products to equilibrium storage level
FLOOD	Acid removed during inundation (lb)
FLOW	Drainage outflow rate (gallon/day)
FLOWMI	Minimum flow rate to cause acid removal by flooding (gallons)
FLSUM	Total acid removal by inundation (lb)
FRAC	Fraction of stored products removed daily during flooding
FSUM	Monthly accumulation of FLOW (gallon/month)
FSUMA	Annual accumulation of FLOW (gallon/year)
FTGMOL	Volume occupied by gm. mole gas (ft^3)
GASC	Gas concentration under mine conditions
GRAVIN	Gravity diffusion into a volume (lb)
GRAVOT	Gravity diffusion out of a volume (lb)
GSUM	Monthly acid removal by gravity diffusion (lb/month)
HEAD	Head of water stored in aquifer (inches)
HEADMI	Minimum flow rate to cause acid removal by leaching
HITE	Height of the layers being executed (ft)
IDAY	Date
IN	Input channel equals to unit 5
IO	Output channel equals to unit 6
IP	Punched output channel equals to unit 7

IY	Identification of year
IYEAR	Year
KAT	Control device in programming
KEEP	Length of month
LAST	Date of previous data input
LTHETA	Days since preceding data input
NDEPTH	Number of depth increments in model
NFEET	Number of air-solid interface increments
NL	Top layer of strata
NLAYER	Number of layers in coal seam model
NPUNCH	Punched output control
OXIDN	Oxidation in a volume (lb)
OXX	Oxygen concentration (mole fraction)
OXY	Oxygen concentration (mole fraction)
PER	Constant value to determine the distance that is inundated
PEVAP	Potential evapotranspiration of each month (inches)
PWATER	Current water storage in root structure (inches)
PWHC	Provisional water holding capacity of root structure (inches)
PYCON	Void fraction of the stratum
RAIN	Rainfall precipitation (inches)
RATE	RAIN/RTIME
RATEK	Reaction rate constants of strata
REACT	Oxygen consumption rate of pyritic material ($\mu g\ O_2 \cdot cm^{-3}$ solid$\cdot hr^{-1}$)
RKEEP	Parameter to stand for RAIN
ROCK	Literal description of strata

RSUM	Monthly accumulation of water entering storage (inches)
RSUMA	Annual accumulation of water entering storage (inches)
RTIME	Duration of rainfall (hr)
RUNOFF	Water runoff from over-burden (inches)
SNOW	Precipitation as snow (inches water)
SOX	Total initial acid storage (lb)
STORE	Oxidation product storage arrays
SWMELT	Amount of melted snow (inches)
TACID	Total acid output based on the three removal mechanisms (lb)
TANK	Aquifer storage (inches)
TEMP	Mine temperature correction factor
THICK	Thickness of strata (ft)
TMEAN	Average daily temperature (°F)
TOP	Datum plane for top of coal seam
TSUM	Accumulation of total acid load (lb)
TYPE	Literal description of strata
UP	Difference in height between layer and water level (ft)
VAP	Monthly potential evapotranspiration value (inches)
WASH	Equilibrium product storage in layer
WATER	Water level relative to the strata (inches)
WOVERW	Fractional saturation of soil, PWATER/PWHC
WSHED	Watershed area of mine (ft^2)
WSLOPE	Slope of the water level during inundation
WSUM	Total acid removed by leaching (lb)
XMAX	Total distance in K-direction (ft)

XMIN	Distance in K-direction that is not flooded (ft)
YSU	Monthly accumulation of acid load (lb/month)
YSUMA	Annual accumulation of acid load (lb/year)

- - - - - -

in the computation model is "J" for the layer number counting upwards from the bottom layer, and "K" for the block number counting in a horizontal direction from the air-solid interface. In addition, the program provides "I" notation for increments along the interface for situations where conditions may vary horizontally along the exposed face.

The quantity of oxidation, which increases the amount of products stored in volume "A" (STORE(I,J,K) in our notation) can be expressed as follows:

$$\mathrm{OXIDN}(I,J,K) = k_R(J)C_{Ox}(I,J,K)\mathrm{DVOL}(I,J,K) \tag{17}$$

OXIDN(I,J,K) is the oxygen consumed per day in a block of volume DVOL (I,J,K). $C_{Ox}(I,J,K)$ is the oxygen concentration in the void volume, and $k_R(J)$ is the rate constant for layer J.

A gravity diffusion function which includes a dependence on the quantity of stored products and which assumes no horizontal motion of products is:

$$\mathrm{GRAVOT}(I,J,K) = \mathrm{DIFFG}(J)\mathrm{STORE}(I,J,K) \tag{18}$$

$$\mathrm{GRAVIN}(I,J,K) = \mathrm{DIFFG}(J+1)\mathrm{STORE}(I,J+1,K) \tag{19}$$

GRAVIN and GRAVOT are the gravity diffusion in and out of a volume, STORE(I,J,K) is the pounds of oxidation products, reported as oxygen consumed, stored in the volume, and "J+1" refers to the volume above. DIFFG(J) is the fraction of products stored in layer J which moves by gravity diffusion each day. For different strata, DIFFG(J) is calculated as a constant fraction, DIF, of the oxidation rate constant. This dependence is based on the assumption that gravity diffusion depends on how fast oxidation products form, and inversely depends on the void volume available for product storage. Both of these factors are included in the rate constant. The magnitude of DIF, 0.01, is chosen to give a net monthly removal rate of about two pounds of acid as described in Section VI. Calculated values of DIFFG(J) are in the range 0.005 to 0.001.

Removal by leaching and flooding are both functions of underground water flows. The leaching occurs as water trickles through channels in the oxidized volume. The trickling water picks up oxidation products and enters the receiving stream. The products which are removed may have been formed either along the flow channel walls or have diffused from adjacent "dry" channels. The basic assumption of the leaching model is that most of the water observed as drainage has not contacted the reactive pyrite volume, but merely dilutes the acid. The reasoning is that if the reactive area were continually washed by large volumes of water, the fine channels in the binder would be filled with water. The water then would block the transport of oxygen to the pyrite, and oxidation would virtually cease.

The quantity of products leached depends both on the amount of products present and on the number of flow channels being utilized for flow. The utilization of flow channels is largely controlled by how much liquid is moving. Therefore, AOUT, the quantity of material leached from a volume may be expressed as a function of the storage contents and the rate of water trickling vertically from the surface:

$$\mathrm{AOUT}(I,J,K) = \mathrm{STORE}(I,J,K) \cdot \mathrm{FJ} \cdot \mathrm{DSLV}. \tag{20}$$

DSLV is the fraction of stored products removed each day by water trickling downward through the binder and pyrite. The value of DSLV has been obtained by correlating the calculated water infiltration rates with observed variations in acid load at the McDaniels Mine. The best match of observed and predicted acid load was obtained for

$$\mathrm{DSLV} = 0.0002*(\mathrm{FLOW}-\mathrm{HEADMI}), \tag{21}$$

where HEADMI is value of FLOW below which no leaching occurs. The term FJ is the ratio of the quantity of stored products to the equilibrium product storage level. The equilibrium storage is the amount of products that would be maintained in an open system where oxidation and removal rates were equal. The equilibrium conditions were estimated by allowing the simulation program to run under conditions of 21 per cent oxygen atmosphere for a three-year period. The quantities of product stored at the end of this period were used as the equilibrium storage.

Acid removal by flushing is mainly due to the rise or movement of the water table. In order to evaluate the flushing mechanism, the water table must first be determined. One method is actual measurement by digging test wells into the hill. Morth[25] obtained an equation to describe the water level of the McDaniels Test Mine by this method. However, this information is not usually available. Furthermore, "the true shape of the water table is not critical for model studies but some form must be selected for computational purposes."[25] For the general case, a different approach can be used.

The water table may intersect the system as shown in Fig. 11. In this table, WSLOPE is the slope of the water level and DEHK is the distance on the bottom layer of the system which is inundated. If the acid removed by flooding is assumed to vary little with WSLOPE, a fixed

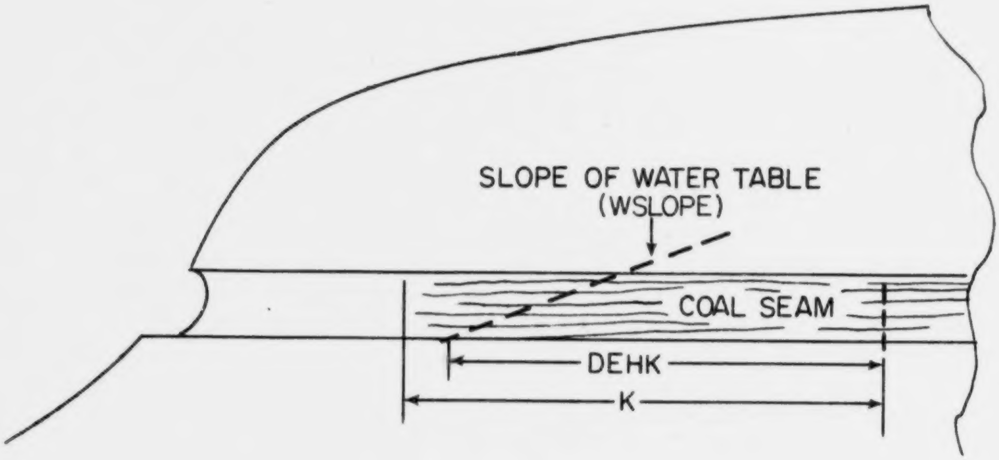

Figure 11 - Location of Water Table

value for WSLOPE can be used and the value of PER selected to match the acid removal contributed by flooding. DEHK is assumed to be a function of FLOW minus a base flow (FLOWMI). This relation is shown in Eq. (22).

$$DEHK = PER*SQRT(FLOW-FLOWMI). \qquad (22)$$

The mean DEHK for a hydrologic year is selected so as to provide enough exposed pyrite to generate the required yearly acid production. If field data are not available, DEHK must be determined by estimating the shape and location of the water table during high and low flow periods. Procedures for evaluating the constants in Eq. (22) are given in Appendix E.

After finding the number of blocks in the system that will be flooded during inundation, the fraction (FRAC) of the acid stored in each block that will be removed each day by this mechanism is calculated. Similar to the leaching mechanism, daily acid removal by flushing can be calculated as the product of STORE and FRAC.

When a storage volume is inundated, the oxidation products gradually dissolve and flow away. The amount of products removed per day is

$$FLOOD(I,J,K) = FRAC \cdot STORE(I,J,K). \qquad (23)$$

FRAC is the fraction of products stored in a volume which are dissolved each day that the volume is inundated. A value of 0.002 per day has been found most appropriate for FRAC. This is a higher value than that of DIFFG (0.0005 to 0.001 range) and that of DSLV (0.0005 to 0.0015 range) since inundation supersedes and includes gravity diffusion and leaching. An upper limit on the rate of removal during inundation arises because of product solubility limitations, and because of the fact that products must still diffuse out of capillary size channels in the inundated volume.

At this point, it is appropriate to discuss in more detail how "suitable" values were obtained for the constants DIF, DSLV, and FRAC. The basis for the evaluation of the constants was the annual acid loads measured at McDaniels Test Mine.

While the three removal mechanisms, leaching, gravity diffusion, and inundation, have been considered as parallel and independent, the total removal must fit the constraints of the observed data. Hence, if one rate is increased, the other two removal rates must be reduced.

In light of the preceding discussion, the general technique for evaluating DIF, DSLV, and FRAC was to pick a value for each and determine how well the annual predictions of acid loads matched the annual loads observed at McDaniels Mine. The key for the initial estimate of the constants was the experimental knowledge that gravity diffusion removed two to four pounds of acid per month combined with an estimate of the total product storage obtained by allowing the program to run for a simulated period of three or four years. The total initial storage was about 150 pounds of acid, and assuming 30 pounds of removal by gravity diffusion per year, a gravity diffusion removal rate of 0.1 pound per day was used. As an order of magnitude estimate, this gave 0.1/150, or about 0.0007 per day for DIF. To get what was essentially a "trial and error" approach started, initial guesses of FRAC and DSLV were set equal to DIF. These values were the right magnitude, but gave low predictions.

The values of the three constants were raised to bring the annual predictions of acid load in line with observed values. Once the annual loads were in line, the "fine tuning" or matching of short-term acid loads was undertaken. The inundation removal term was the most sensitive of the three rates during the first three months of the year. It is, in process control terminology, a derivative function which responds rapidly to changes in the water table. Hence, the inundation constant FRAC could be used to match early year increases in acid load. The leaching constant DSLV is most important in times of high flow so it could be varied to produce the best acid load predictions in April, May, and June.

As each constant was varied, the other two also had to be adjusted. During the general trial and error evaluation, it was observed that any constant could be varied by 30 or 40 per cent of its value without great damage to the annual prediction capability of the model. However such variations in FRAC or DSLV could shift short-term prediction peaks by as much as 3 or 4 weeks.

Once all the events probable in a given volume have been defined, the appropriate terms are summed to give the new storage contents in the volume. Under normal circumstances (no flooding) the new product storage in a volume is the sum of the rates in Eqs. (17-20) plus the previous storage:

$$\mathrm{STORE(I,J,K) = STORE(I,J,K) + OXIDN(I,J,K) + GRAVIN(I,J{+}1,K) - GRAVOT(I,J,K) - AOUT(I,J,K)}. \tag{24}$$

During inundation, the water forms an oxygen diffusion barrier so that oxidation virtually ceases, and

$$\mathrm{STORE(I,J,K) = STORE(I,J,K) - FLOOD(I,J,K)}. \tag{25}$$

The total acid removed from the system is the sum of all AOUT(I,J,K), and FLOOD(I,J,K) where appropriate, terms plus the GRAVOT terms from storage volumes immediately above the water table. The calculation of acid load as the sum of all acid removal rates assumes that oxidation products leave the mine as soon as they enter the ground water. The summation of all these removal terms plus the calculation of new storage quantities are performed by a digital computer. The computer program which does these calculations iteratively to simulate the passage of time will be described in the following section.

COMPUTER PROGRAMMING OF MODEL

The programming of this or any other model is the restatement of regular mathematical equations in the particular form required by a digital computer. This language of the computer has already been introduced with the I,J,K notation at the beginning of this section. The computational model of the drift mine will be described in terms of one main program and three sub-routines. The main program maintains generality with regard to most pyritic systems, but the subroutines include special provisions for a specific mine site. A flow chart for the main program is shown in Fig. 12, and flow charts for the subroutines are shown in Figs. 13, 14, and 15.

The main program has two principal sections. The first section handles bookkeeping such as defining variables, establishing computational arrays, and setting initial values. The arrays are the subscripted variables which represent incremental changes in distances or conditions in different locations. The initial conditions to be established include a base datum plane, a minimum water level datum, dimensions of the coal and shale strata, alkalinity of ground water, the "water shed" area drained by the mine, experimental or estimated oxidation rates, and conversion factors. The most critical set of initial values is the

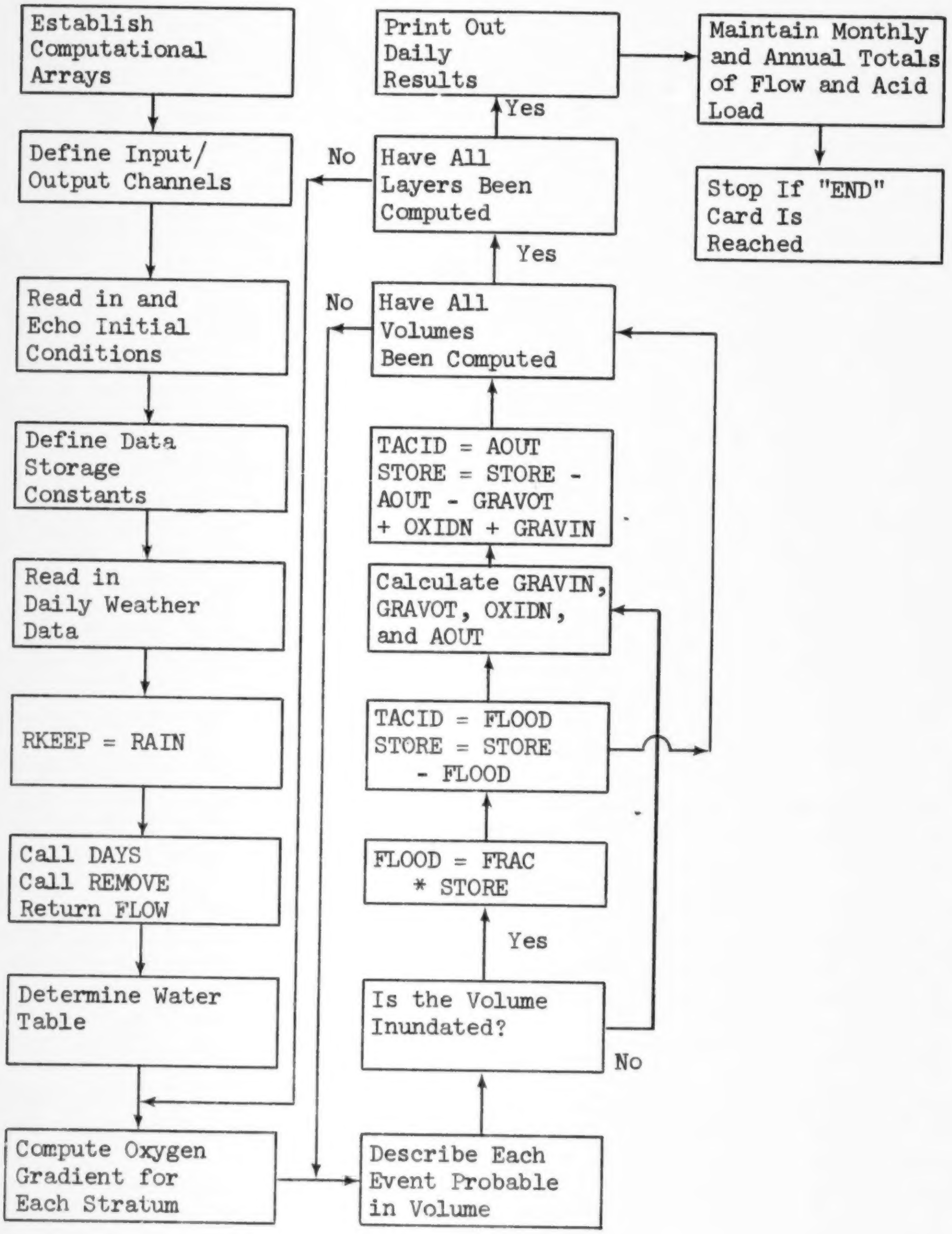
Establish Computational Arrays
Define Input/ Output Channels
Read in and Echo Initial Conditions
Define Data Storage Constants
Read in Daily Weather Data
RKEEP = RAIN
Call DAYS Call REMOVE Return FLOW
Determine Water Table
Compute Oxygen Gradient for Each Stratum
Describe Each Event Probable in Volume
Is the Volume Inundated?
No
Yes
FLOOD = FRAC * STORE
TACID = FLOOD STORE = STORE - FLOOD
Calculate GRAVIN, GRAVOT, OXIDN, and AOUT
TACID = AOUT STORE = STORE - AOUT - GRAVOT + OXIDN + GRAVIN
Have All Volumes Been Computed
No
Yes
Have All Layers Been Computed
No
Yes
Print Out Daily Results
Maintain Monthly and Annual Totals of Flow and Acid Load
Stop If "END" Card Is Reached

Figure 12 - Main Program Flow Chart

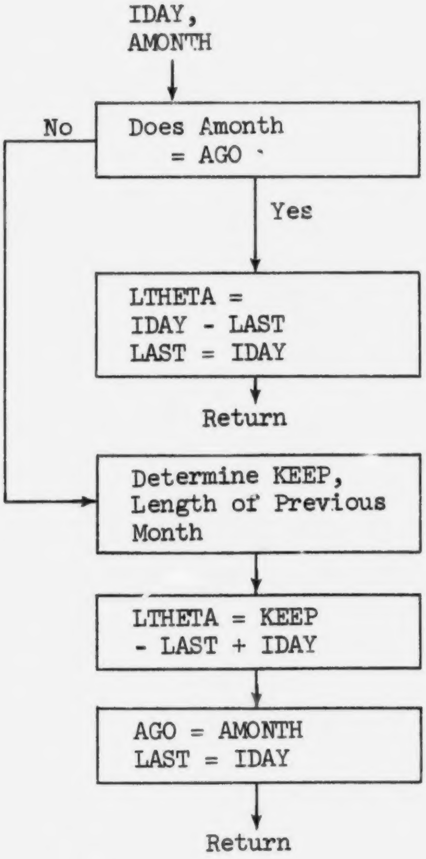
IDAY,
AMONTH
No
Does Amonth
= AGO
Yes
LTHETA =
IDAY - LAST
LAST = IDAY
Return
Determine KEEP,
Length of Previous
Month
LTHETA = KEEP
- LAST + IDAY
AGO = AMONTH
LAST = IDAY
Return

Figure 13 - Flow Chart of Subroutine DAYS

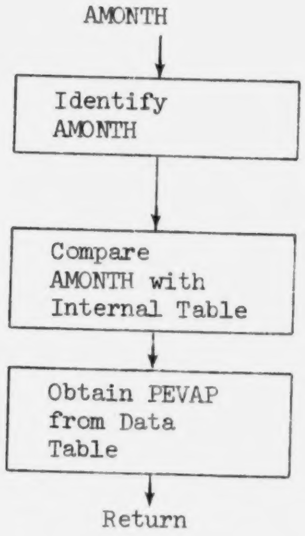
AMONTH
Identify AMONTH
Compare AMONTH with Internal Table
Obtain PEVAP from Data Table
Return

Figure 14 - Flow Chart of Subroutine EVAP

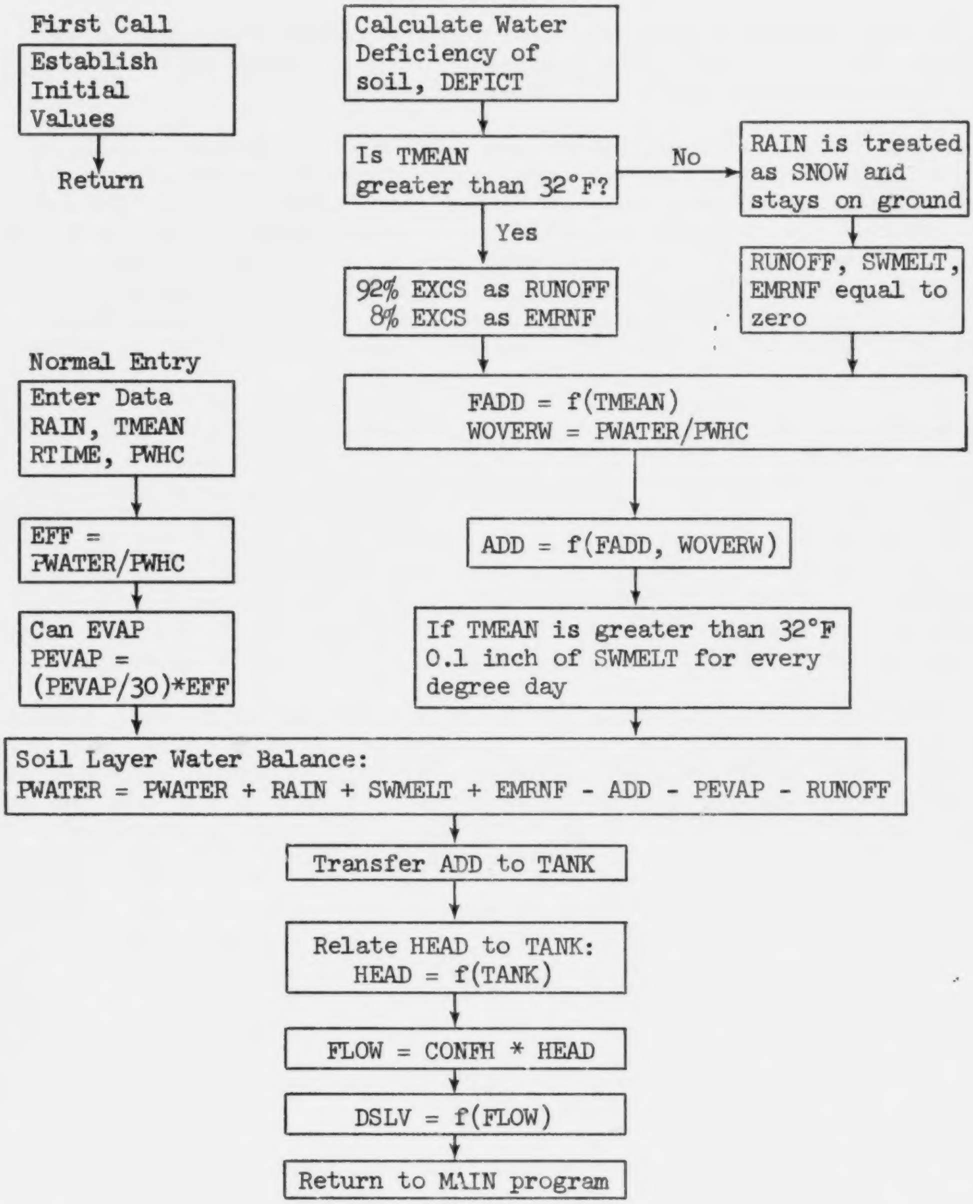
First Call
Establish Initial Values
Return
Calculate Water Deficiency of soil, DEFICT
Is TMEAN greater than 32°F?
No
RAIN is treated as SNOW and stays on ground
Yes
92% EXCS as RUNOFF
8% EXCS as EMRNF
RUNOFF, SWMELT, EMRNF equal to zero
Normal Entry
Enter Data RAIN, TMEAN RTIME, PWHC
FADD = f(TMEAN)
WOVERW = PWATER/PWHC
EFF = PWATER/PWHC
ADD = f(FADD, WOVERW)
Can EVAP PEVAP = (PEVAP/30)*EFF
If TMEAN is greater than 32°F 0.1 inch of SWMELT for every degree day
Soil Layer Water Balance:
PWATER = PWATER + RAIN + SWMELT + EMRNF - ADD - PEVAP - RUNOFF
Transfer ADD to TANK
Relate HEAD to TANK:
HEAD = f(TANK)
FLOW = CONFH * HEAD
DSLV = f(FLOW)
Return to MAIN program

Figure 15 - Flow Chart of Subroutine REMOVE

estimate of oxidation products stored in the system from previous oxidation. That is to say, we are breaking into a "steady state" system, and the steady state point is nonzero in value.

To obtain initial storage values, the computer program was allowed to run for a simulated period of three years of oxidation and removal. The oxidation rates were based on 21 per cent oxygen level in the mined-out volume since prior to the start of the observation period, McDaniels Mine had been open to the atmosphere. The final storage values, STORE(I,J,K), were then punched out on standard computer cards in a format suitable for reading-in as data. Once the initial conditions have been established, the simulated daily mine behavior can be calculated.

The second section of the program, which does the day-to-day simulation, will be described in terms of a typical run. The first step in the simulation is the reading of meteorological data. The date, the inches of precipitation, hours of duration of precipitation, mean daily temperature, and oxygen concentration at the air-solid interface are the input data. The program is written in such a manner that only positive information such as precipitation or changes in the temperature or oxygen level need be read in. The input data are examined to determine if any conditions have changed, and the amount of precipitation is recorded.

The subroutine "DAYS" is called to determine the number of days, LTHETA, since the previous data input. The program is run on the condition that precipitation occurs only on the LTHETA day--whether this is one day or one month from the previous precipitation. The program performs the following set of calculations for each day. The computer variables introduced in this section are summarized in Table 2.

1. The subroutine "REMOVE" is called. This routine, described later in more detail, calculates the ground flow and the quantity of water in underground storage. The factor DSLV, the fraction of stored products removed each day by leaching, is also returned by "REMOVE."

2. The position of the water table in relation to the coal seam is calculated from Eq. (22).

Steps 1 and 2 have furnished numerical information for calculating product removal rates. The next steps are performed iteratively over the computer array of oxidation storage volumes, STORE(I,J,K), for all volumes above the water table. For inundated volumes, the program skips to Step 7.

3. The oxygen mole fraction, XNN, in the void volume is determined using the oxygen gradient equation [Eq. (7)]. The total volume of the block, DVOL, is calculated. The oxidation, as pounds of oxygen consumed per day, is determined.

4. The quantity of products removed by leaching, AOUT, is calculated using Eq. (20).

5. The gravity diffusion in, GRAVIN, and out, GRAVOT, are computed using Eqs. (18) and (19).

6. The terms calculated in Steps 3, 4, and 5 are summed to obtain the change in product storage. The program then skips to Step 8.

7. The quantity of products removed from an inundated volume is obtained from Eq. (23). Since there is no oxidation in inundated volumes, the new storage quantity is calculated simply by subtracting the quantity removed from the product storage value.

8. The quantity of acid removed from each storage volume is added to the running total, TACID, of acid removed. In addition, sub-totals of the amount of acid removed by each mechanism are also kept.

After the calculations have been performed for all of the volumes of the STORE(I,J,K) array, the results are prepared for output.

9. The acid load, TACID, is converted from an oxygen consumption to a "total acid" basis by multiplying by 200/112. This is the stoichiometric ratio of 2 H_2SO_4 to 7/2 O_2 when acidity is expressed as the calcium carbonate ($CaCO_3$) equivalent.

10. The acid load is then corrected for the influence of alkalinity in the entering ground water. A value of 20 ppm alkalinity has been used for the McDaniels Mine.

11. The daily acid load is added to the cumulative monthly, YSUMA, and annual YSUM, acid load totals. Similarly, monthly totals of removal by gravity diffusion, GSUM, inundation, FSUM, and leaching, ASUM, are also accumulated.

12. The daily flow, acid load, and precipitation are printed. At the end of each month, a summary including flow, total acid load, inches of water entering underground storage, and the acid removed by each mechanism is printed.

13. Similarly, annual or quarterly summaries may be printed. The sample program in Appendix C shows monthly and annual summaries.

Once the calculations have been performed for one day, the program repeats Steps 1 through 12 LTHETA times. On the LTHETA day, the call of the "REMOVE" subroutine includes the amount of precipitation. "REMOVE" performs all calculations involving rainfall and ground water flows.

Several subroutines have been written to assist the main program. The subprograms were written for either of two reasons. First, some routines are of general use so it is convenient to be able to move them from one main program to another. Second, each subroutine is compiled independently. This feature can greatly simplify "debugging" and identification of errors in the program. Errors can be corrected immediately rather than propagating and giving false error messages in unrelated portions of the program.

The subroutine "DAYS" determines the number of days between two consecutive data inputs. The name of the month and the date are read into the routine which compares the name of the month with the name of the month from the preceding input. If the names of the months are the same, the routine obtains the difference of the two dates and returns this as the elapsed time, LTHETA. If the months are different, the routine determines the number of days in the preceding month from an internal data table. The old date is subtracted from the month length. The difference is added to the new date to give LTHETA. The "DAYS" subroutine simplifies data input since only positive information or changes in conditions need be read because the time between changes can be computed. "DAYS" is a general routine that can be transferred from program to program.

The subroutine "EVAP" determines the potential evapotranspiration at the McDaniels Test Mine. Monthly evapotranspiration rates have been calculated according to the Thornthwaite and Mather[42] technique. These values are read into the main program as data and transferred to the subroutine through a common statement. The call to the subroutine includes the name of the month. "EVAP" finds the evapotranspiration rate corresponding to the month from an internal data table, and returns this value to the calling program. This routine can be used for other sites if the appropriate evapotranspiration rates are calculated or measured and supplied to the program.

Subroutine REMOVE

The major subroutine is "REMOVE," which has been written to calculate drainage flow rates. The program also determines the fraction of stored products to be removed each day by leaching.

On the first call of "REMOVE," initial conditions are established. An estimate of TANK is made and the program allowed to run for 3 to 5 years to obtain an initial value of TANK. On each succeeding call, the following operations are performed:

1. Daily potential evapotranspiration is determined. The monthly maximum evapotranspiration is obtained by calling

"EVAP." This value is converted to a daily value by dividing by the days per month. The daily value is reduced according to the moisture content of the soil layer.

2. The water deficiency in root storage, DEFICIT = PWHC - PWATER, is calculated.

3. The Soil Layer Water Balance is made:

   A. If there has been rainfall or snow melting for the day, the precipitation (RAIN) is compared to DEFICT. If RAIN is greater than DEFICT, 92% of the excess rain (EXCESS) goes to runoff; the remainder to the soil layer (EMRNF). If RAIN is less than DEFICT, all precipitation enters soil layer.

   B. The mobility of water in the soil layer, as denoted by FADD, is determined from the mean temperature for the day (see Appendix E).

   C. The ratio of water in the soil layer to the saturated water content (PWATER/PWHC = WOVERW) is calculated.

   D. ADD, the water leaving the soil layer to aquifer storage (TANK), is calculated as a function of FADD and WOVERW [Eq. (27a) and (27b), Appendix E].

   E. The new value for PWATER is calculated from the water balance on the soil layer [Eq. (16)].

4. The new daily value for aquifer storage (TANK) is determined as the addition of ADD minus the loss from storage due to flow from the mine (FLOW).

5. DSLV, the fraction of stored products removed by leaching is then calculated using Eq. (21).

SECTION VIII

VERIFICATION OF MODEL

The validity of the model can be evaluated by using the model to simulate mine drainage behavior for a period during which there are natural data. Such a comparison has been made for the McDaniels Test Mine, the auger holes, and the Decker No. 3 mine.[22]

The computer program was run using the physical description of the mines and meteorological data as inputs. The experimental variations of oxygen in the mine atmosphere were also included in the data. The output from the program was the daily drainage, in gallons, and the acid load, in pounds. In addition, monthly and annual totals of drainage and acid load were printed.

The day-by-day predictions of the model have been graphically compared with the natural observations. The drainage flow rates are shown in Figs. 16-22, and the acid loads are compared in Figs. 23-29. A hydrologic year beginning with the October dry season has been used as the time basis. This choice simplifies visualization of the cyclic nature of acid mine drainage rates.

The data in Figs. 16-29 show the capability of the model to predict the sharp peaks of drainage and acid load in the spring of each year. Likewise, the figures show the steady decline of flow rates through the summer and fall. The success of the model in predicting short-term variations has fulfilled a major objective of this investigation. Such a short-term response is necessary if the model is to be used to predict peak loads for use in the design of treatment facilities. Similarly, the operation of existing treatment plants may require knowledge of when peak acid loads will occur.

While the agreement of predicted and observed short-term data is desirable, the validity of the model in the general case may depend more on the long range predictions. Tables 3-8 summarize the monthly and annual (on a calendar year basis) drainage flows and acid loads. In these tables it can be seen that monthly predictions are generally within 20 per cent of the measured rates, and that annual values agree within 5 per cent. The goodness of fit of long-term data is important since there were large year-to-year variations in acid load because of the variation of oxygen levels in the mine atmosphere.

The practical significance of the agreement of long-range predictions and observations is that for unmanned treatment facilities in isolated areas, the model could be used to estimate the quantity of treatment chemicals which must be available. The model can also estimate how often the chemicals must be replenished.

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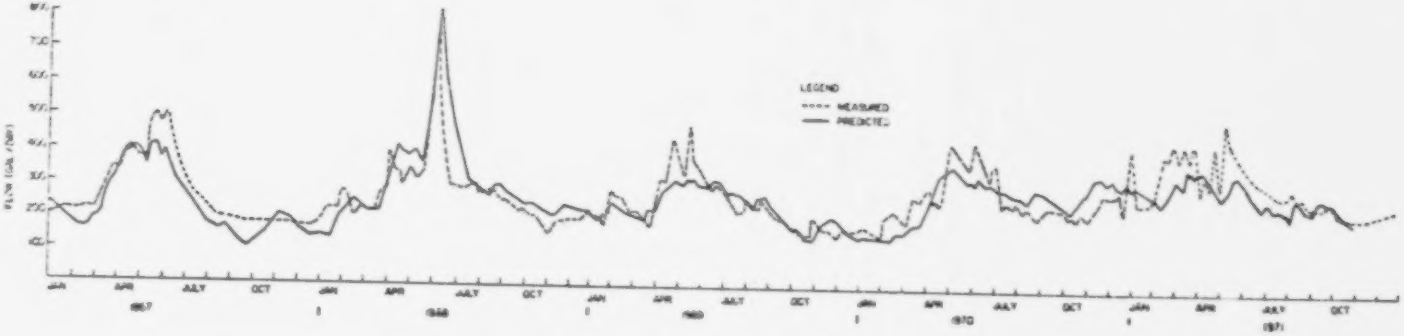

Figure 16 - Drainage Flow for McDaniels Test Mine

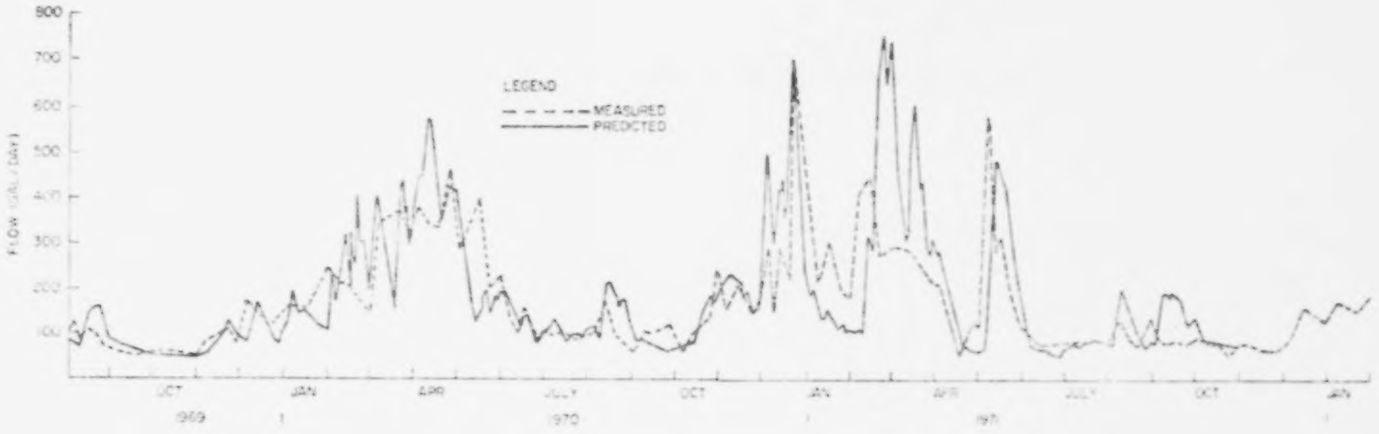

Figure 17 - Drainage Flow for Auger Hole #1

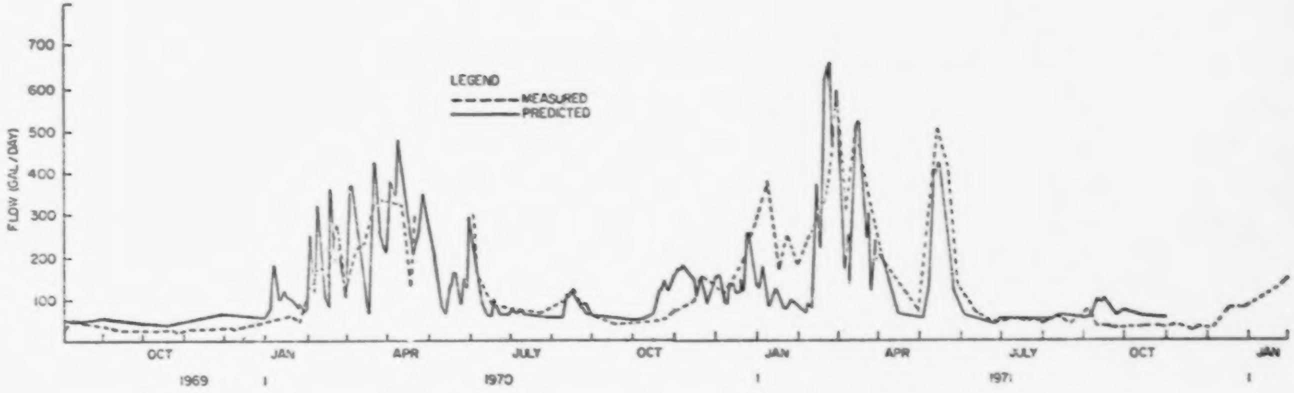

Figure 18 - Drainage Flow for Auger Hole #3

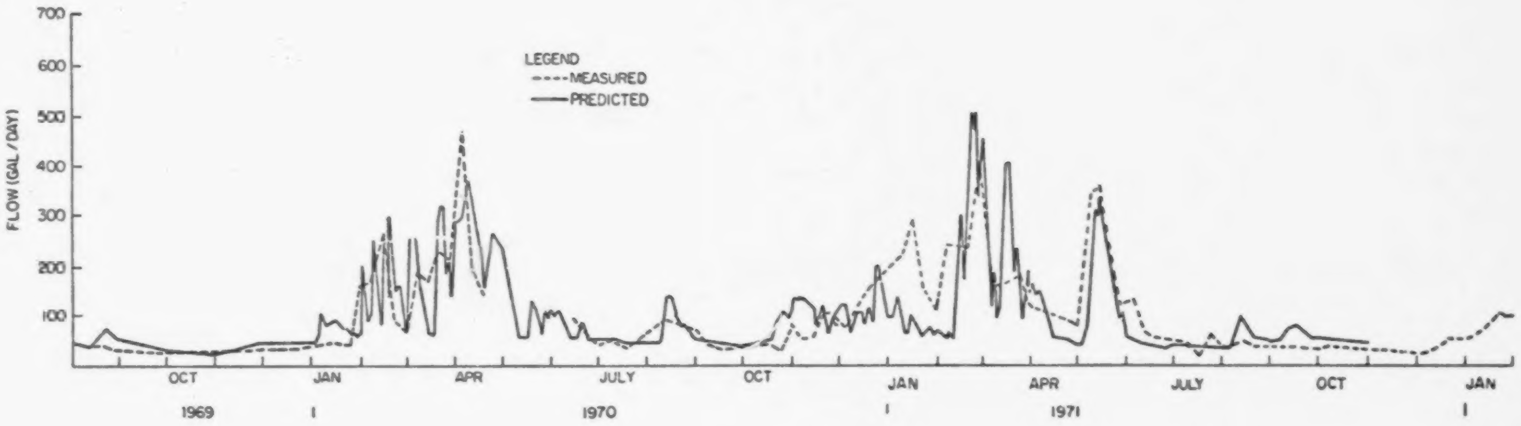

Figure 19 - Drainage Flow for Auger Hole #4

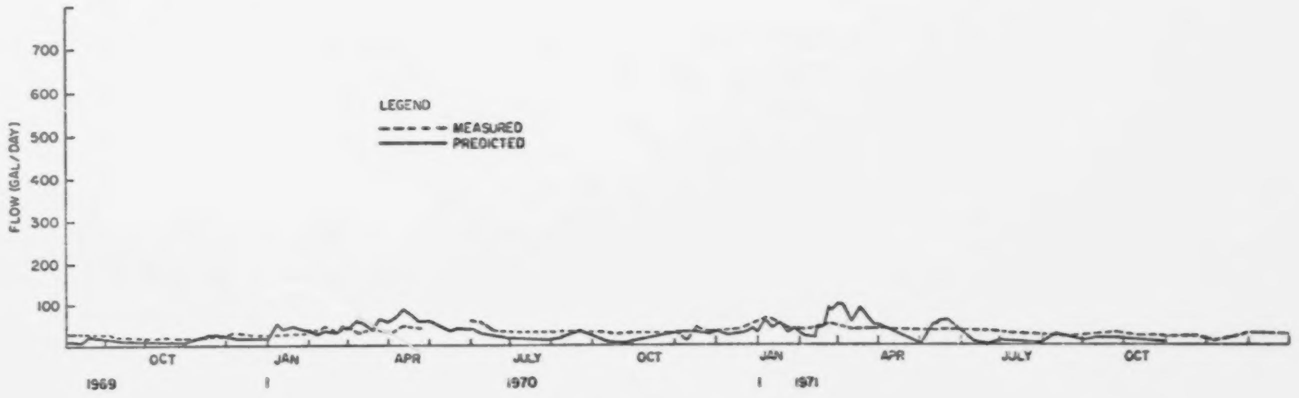

Figure 20 - Drainage Flow for Auger Hole #5

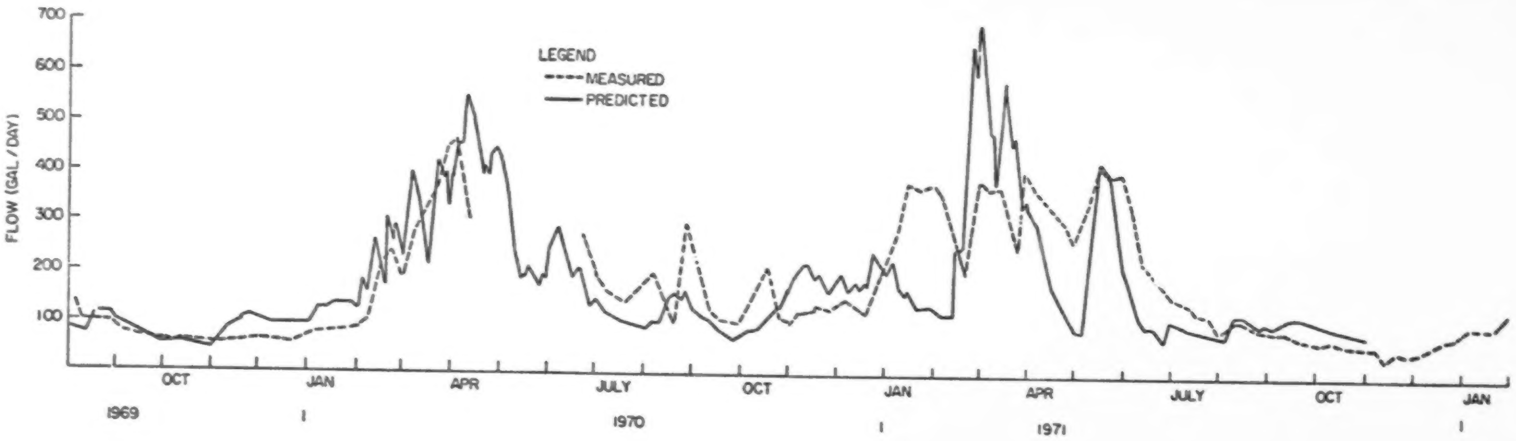

Figure 21 - Drainage Flow for Auger Hole #6

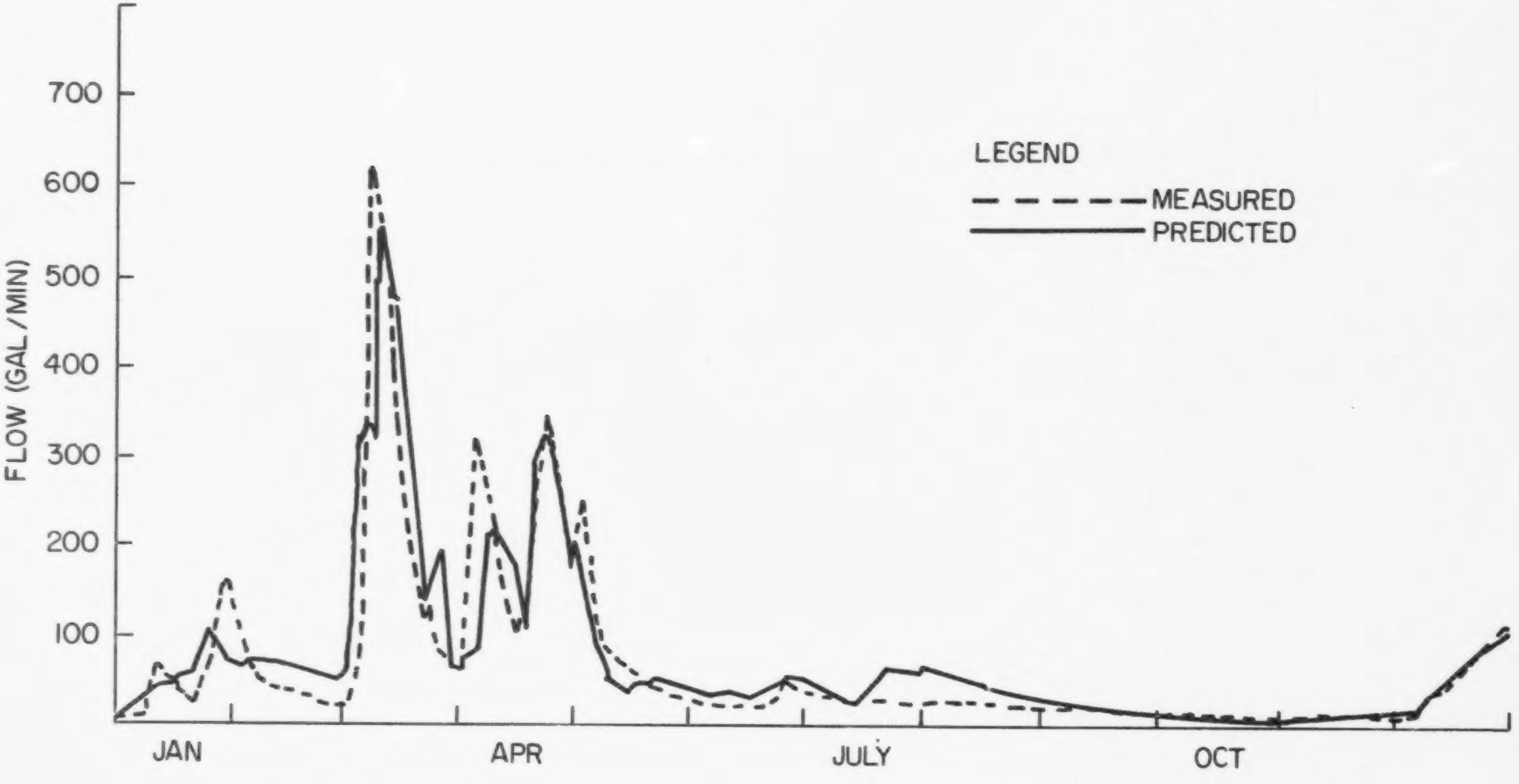

Figure 22 - Drainage Flow for Decker #3 Mine (1964)

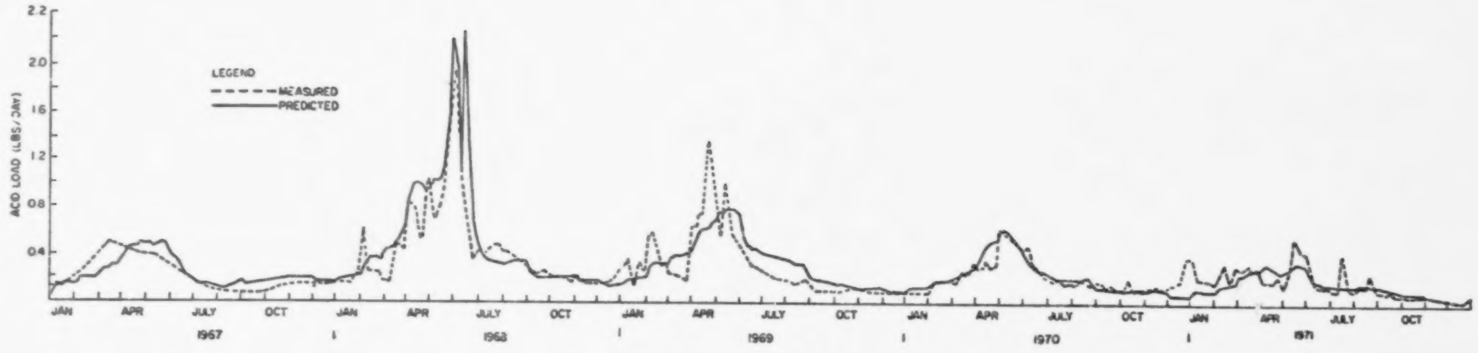

Figure 23 - Acid Load for McDaniels Test Mine

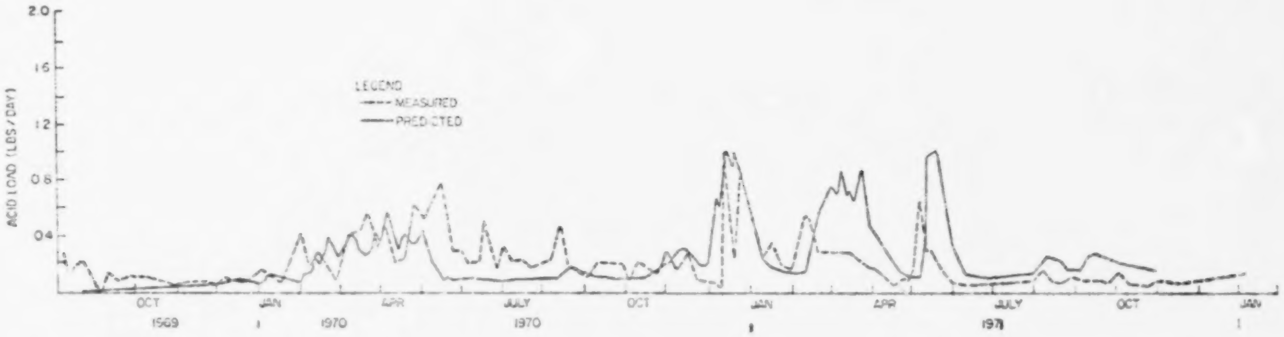

Figure 24 - Acid Load for Auger Hole #1

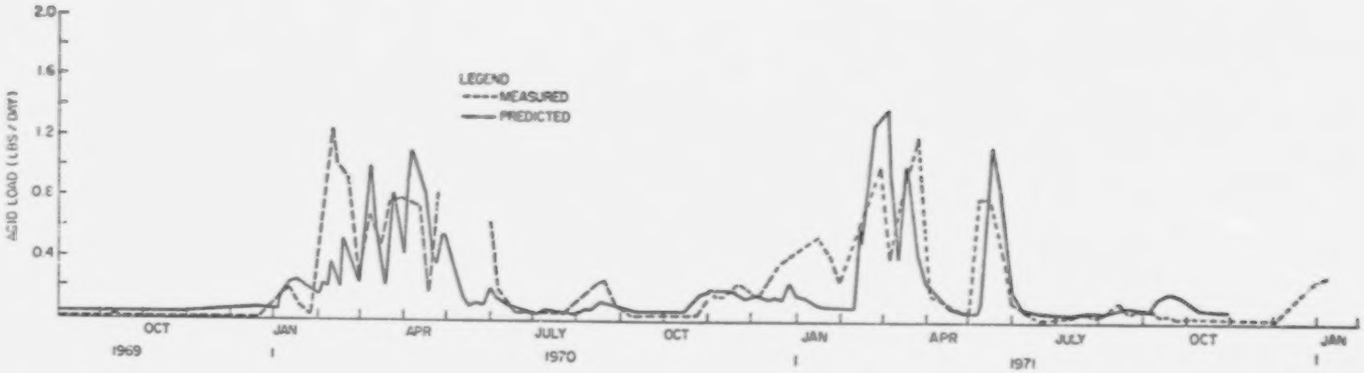

Figure 25 - Acid Load for Auger Hole #3

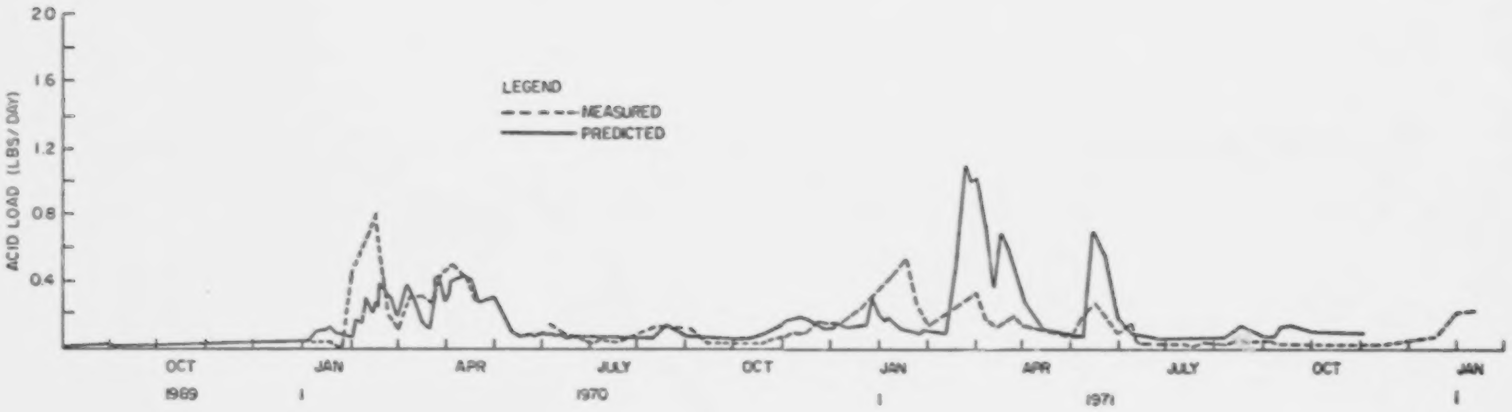

Figure 26 - Acid Load for Auger Hole #4

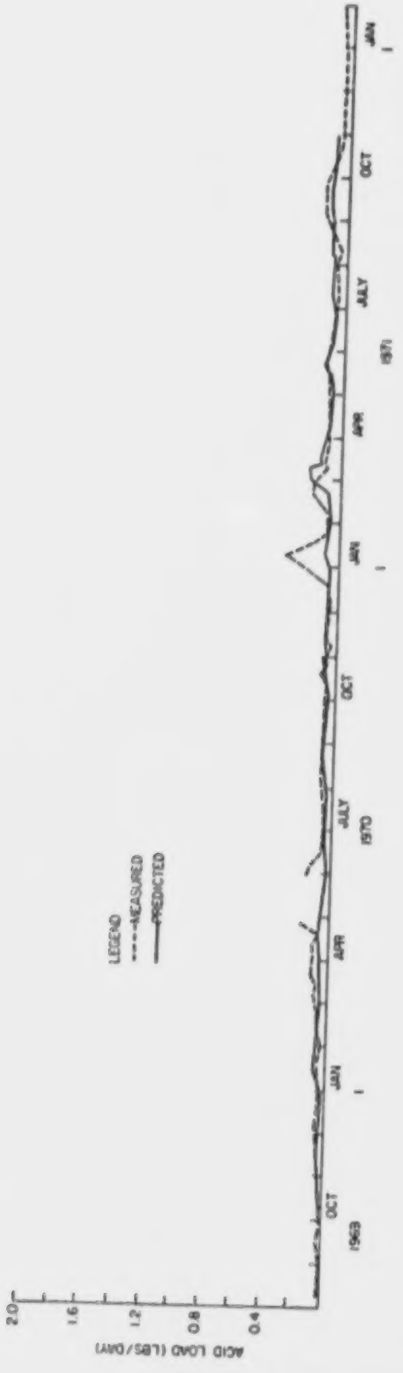

Figure 27 - Acid Load for Auger Hole #5

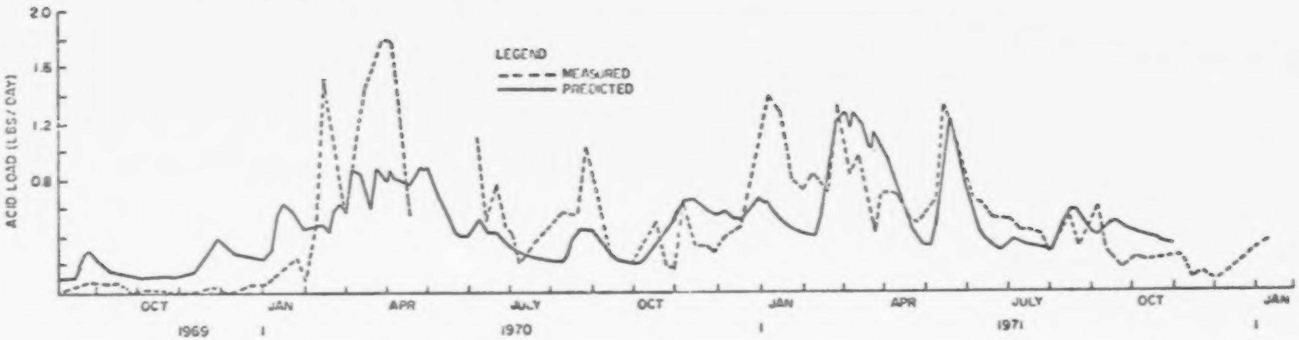

Figure 28 - Acid Load for Auger Hole #6

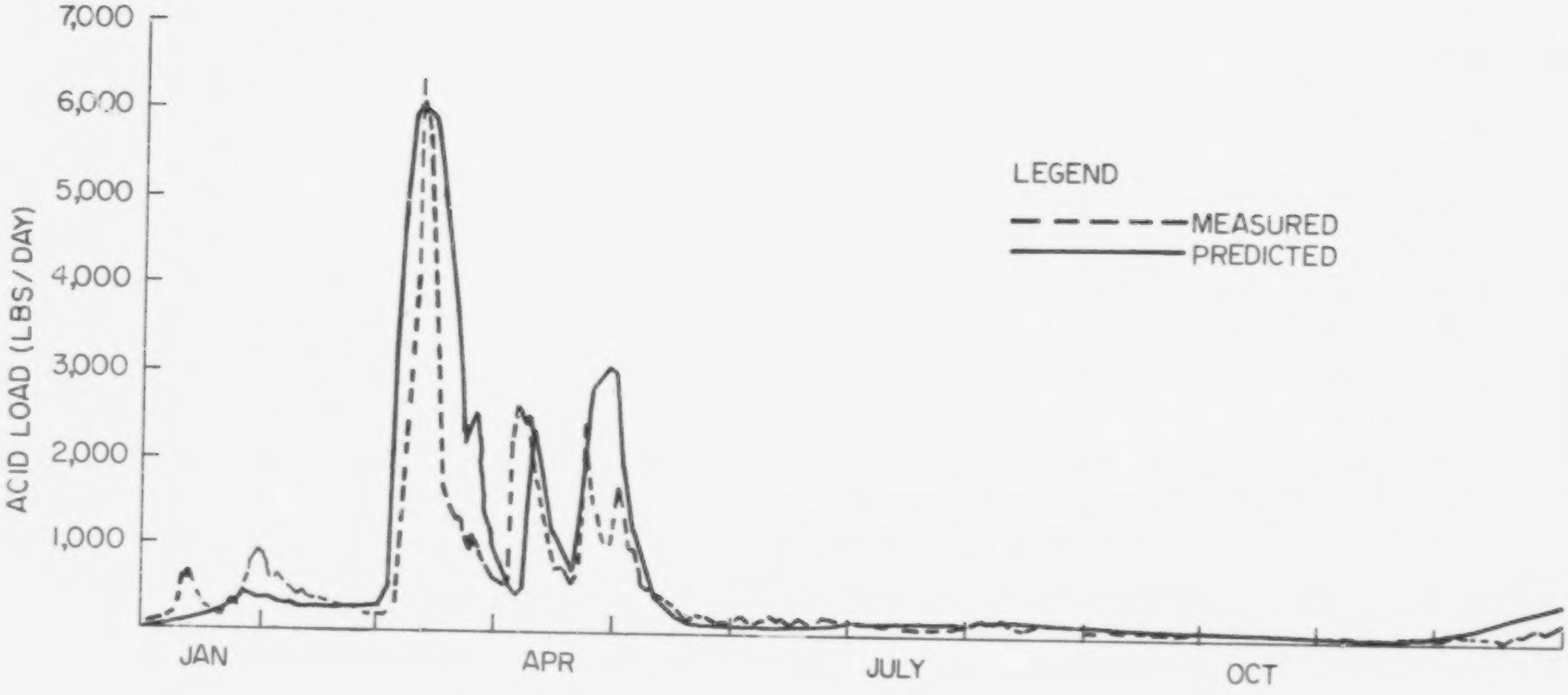

Figure 29 - Acid Load for Decker #3 Mine (1964)

TABLE 3

DRAINAGE FLOW RATES FOR MCDANIELS TEST MINE

	1967		1968		1969		1970		1971	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	6,510	6,473*	7,560	5,256	6,780	6,669	5,850	4,921	8,250	9,094
February	6,300	4,910	6,090	6,685	7,200	6,500	6,100	4,734	10,500	7,834
March	8,700	8,049	7,510	7,986	6,920	6,602	9,000	6,544	12,450	10,592
April	11,250	11,766	10,350	12,077	11,250	8,456	9,870	9,819	10,500	9,905
May	13,800	12,506	16,300	15,673	12,000	9,824	11,780	10,371	13,500	9,871
June	12,150	11,857	8,610	16,982	9,030	9,493	9,600	9,600	9,900	8,266
July	7,500	7,953	8,700	10,145	8,100	8,763	8,740	8,828	9,000	7,757
August	6,150	6,004	8,500	9,034	7,240	8,253	7,690	8,866	8,250	7,964
September	5,700	4,264	7,000	7,679	5,730	6,477	7,290	7,556	7,500	8,056
October	5,400	5,163	6,360	6,931	5,680	5,101	6,940	8,060	6,900	7,169
November	5,250	6,163	5,670	6,488	5,520	5,816	8,100	9,850	7,200*	-
December	5,400	5,181	6,550	7,095	5,400	5,443	9,300	9,819	7,300*	-
Total	94,110	90,289	99,000	112,031	89,000	88,397	99,000	98,965	97,550	86,505

* Not included in the annual total.

TABLE 4

DRAINAGE FLOW RATES FOR AUGER HOLES 1, 3, 4, 5, 6

1970	Auger Hole #1		Auger Hole #3		Auger Hole #4		Auger Hole #5		Auger Hole #6	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	6,014	4,324	2,325	3,074	2,211	2,217	775	1,156	2,604	3,952
February	5,376	7,262	5,208	5,099	4,890	4,326	810	1,024	5,208	6,392
March	10,912	9,975	9,556	8,023	6,060	5,822	1,115	1,613	10,788	10,848
April	10,050	13,535	10,140	10,097	8,130	7,781	1,200	2,100	11,430	14,139
May	8,742	6,507	-	4,622*	-	3,241*	-	1,132*	-	7,700*
June	3,690	4,148	3,750	3,010	4,110	2,224	1,235	686	9,690	6,523
July	3,069	3,263	2,139	1,932	1,350	1,580	868	412	5,177	3,500
August	4,061	4,848	2,914	2,555	2,449	2,505	930	729	9,393	4,254
September	2,970	2,294	1,290	1,676	1,410	1,415	750	301	3,540	2,925
October	4,876	3,762	1,454	2,829	1,550	2,188	1,240	604	4,433	3,341
November	5,430	6,039	3,570	4,405	2,460	3,405	865	941	4,020	6,095
December	10,509	12,734	4,526	4,554	3,689	3,521	1,155	938	4,260	6,311
Total	75,690	78,690	46,875	47,255	38,309	36,984	10,943	10,502	70,543	68,276

TABLE 4 - (Continued)

1971	Auger Hole #1		Auger Hole #3		Auger Hole #4		Auger Hole #5		Auger Hole #6	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	7,099	4,479	7,595	3,132	6,107	2,412	1,630	1,265	11,191	5,208
February	10,892	10,407	9,300	8,933	8,624	6,965	1,180	1,369	9,100	9,533
March	8,184	13,301	15,640	8,787	5,208	6,745	1,366	2,149	11,191	14,652
April	4,020	4,583	4,440	3,014	3,150	2,376	1,080	807	10,500	5,839
May	11,556	9,077	8,928	6,753	6,913	5,159	1,085	1,370	11,501	8,849
June	2,670	2,126	1,950	1,534	2,760	1,256	960	342	7,920	3,387
July	2,278	2,449	1,519	1,578	1,426	1,257	750	366	4,154	2,996
August	3,450	3,991	1,612	1,822	1,395	1,852	735	601	3,534	3,594
September	2,550	4,688	1,200	2,499	1,050	1,892	750	555	2,520	3,608
October	2,250	2,480	900	1,915	1,110	1,567	720	394	2,100	3,120
November	2,250*	-	930*	-	750*	-	600*	-	1,650*	-
December	3,780*	-	1,950*	-	1,200*	-	450*	-	2,250*	-
Total	56,379	57,582	53,084	39,964	37,743	31,481	10,256	9,219	63,711	60,786

* Not included in the annual total; units are in gallons.

TABLE 5

DRAINAGE FLOW FOR DECKER #3 MINE

1964	Actual (gal/1440)	Actual (gal/1440)
January	1,856	1,626
February	1,305	1,761
March	6,591	8,248
April	5,394	5,642
May	2,588	2,099
June	901	1,279
July	706	1,558
August	642	1,597
September	438	519
October	293	287
November	241	346
December	1,547	1,974
Total	22,502	29,287

TABLE 6

ACID LOAD FOR MCDANIELS TEST MINE*

	1967		1968		1969		1970		1971	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	4.5	4.0	5.7	6.3	7.9	6.0	3.1	4.2	6.1	3.0
February	7.6	5.2	9.5	9.9	12.7	8.8	5.2	5.4	7.0	4.3
March	13.8	8.6	12.6	15.6	9.7	12.4	8.5	8.7	8.7	8.3
April	12.6	13.7	23.0	28.9	25.4	18.3	12.5	14.9	5.4	9.2
May	11.2	15.0	39.5	39.8	20.7	23.9	14.9	17.2	11.4	9.8
June	7.5	8.5	16.8	42.7	10.2	14.7	7.7	9.3	5.3	5.6
July	4.2	4.4	12.4	11.3	6.7	12.1	5.1	7.5	5.7	4.8
August	2.4	4.2	11.4	10.4	5.0	9.8	5.0	6.5	4.1	4.9
September	2.3	4.5	7.2	6.6	3.2	5.8	3.7	3.7	2.4	3.1
October	3.0	5.7	5.5	6.4	3.4	4.9	3.9	3.8	2.1	2.8
November	4.2	5.9	4.8	5.4	2.8	4.1	4.1	3.9	1.5**	-
December	4.3	5.2	5.4	4.6	2.5	3.4	6.9	2.5	1.1**	-
Total	77.6	84.9	154.0	187.9	112.0	124.2	80.6	88.0	58.2	56.0

* Units are in pounds.
**Not included in the annual total.

TABLE 7

ACID LOAD FOR AUGER HOLES 1, 3, 4, 5, 6*

1970	Auger Hole #1		Auger Hole #3		Auger Hole #4		Auger Hole #5		Auger Hole #6	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	5.1	2.6	4.2	5.9	2.1	2.7	1.2	2.0	4.5	15.8
February	6.3	6.9	22.9	8.3	14.9	7.0	1.8	1.5	21.0	14.8
March	12.0	10.3	19.5	17.3	9.0	9.3	2.7	1.5	39.5	24.1
April	12.1	12.1	11.1	22.4	11.2	10.9	3.3	1.6	-	25.2**
May	16.2	5.1	-	5.4**	-	3.8**	-	1.1**	-	17.0**
June	8.3	2.7	3.3	2.8	2.4	2.1	2.7	1.0	-	13.7**
July	3.7	2.6	1.6	1.6	1.5	1.7	1.5	1.0	10.5	8.5
August	6.3	4.1	5.4	2.7	3.0	2.8	2.4	1.5	20.3	11.1
September	5.1	3.0	1.5	1.7	1.8	1.8	2.2	1.2	11.7	8.8
October	4.5	4.1	1.5	3.1	1.5	2.6	2.4	1.7	9.6	10.6
November	4.8	7.4	5.4	5.1	3.0	4.4	1.5	2.0	11.7	17.9
December	14.1	24.6	8.4	4.8	6.0	4.8	2.7	1.7	17.1	17.3
Total	98.5	85.0	84.8	75.3	56.4	50.1	24.4	16.5	155.9	128.9

TABLE 7 - (Continued)

1971	Auger Hole #1		Auger Hole #3		Auger Hole #4		Auger Hole #5		Auger Hole #6	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
January	9.0	6.4	13.8	3.4	10.5	3.5	5.7	2.0	33.6	15.8
February	11.7	10.5	18.3	17.1	6.9	13.7	3.9	2.3	27.6	19.5
March	7.8	22.0	24.0	22.7	5.1	17.3	3.0	4.0	23.3	36.0
April	3.0	6.4	3.6	3.5	3.0	4.3	1.9	2.0	18.0	18.6
May	7.8	16.6	15.6	15.5	5.4	11.3	2.7	2.7	27.9	24.6
June	2.0	3.9	1.5	2.2	1.5	2.5	1.9	1.8	17.1	11.9
July	2.0	3.6	1.2	1.8	0.8	2.2	1.5	1.9	12.6	10.0
August	3.0	5.9	2.4	2.3	0.9	3.2	2.1	2.6	12.0	14.1
September	2.7	6.7	1.5	4.5	0.8	3.4	4.0	2.7	9.0	13.5
October	2.1	4.9	0.6	2.9	0.7	3.0	2.1	2.3	6.3	11.5
November	1.9**	-	0.5**	-	0.9**	-	2.1**	-	3.2**	-
December	3.0**	-	4.2**	-	3.0**	-	2.2**	-	5.4**	-
Total	51.1	87.0	82.5	76.0	35.6	64.0	28.8	24.0	187.4	175.0

* Units are in pounds.
**Not included in the annual total.

TABLE 8

ACID LOAD FOR DECKER #3 MINE

1964	Actual (lb)	Predicted (lb)
January	10,793	7,428
February	11,442	10,114
March	58,360	111,036
April	39,672	46,298
May	15,300	15,485
June	5,076	33,181
July	3,802	4,373
August	3,545	5,482
September	2,797	2,933
October	1,973	2,389
November	1,800	2,640
December	3,399	8,546
Total	167,959	219,900

A word of warning should be issued before the model is strongly praised or condemned for the level of agreement with the natural data. The natural measurements are based on flow samples collected once or twice each week. Obviously, the reliability or the comparison would be improved if sampling frequency were increased.

When the acid removal was discussed in Section VI, the description of three different removal mechanisms was emphasized. The importance of each of these mechanisms in the actual simulation is shown in Table 9. The annual acid loads are compared with the quantity of acid removed by each method. (The annual totals in Table 9 are less than the sums of the three separate rates since only the total includes the influence of alkalinity in the ground water. For the case of 20 ppm alkalinity in the water, the acid reduction is about 17 lb/year for 100,000 gallons of flow.)

TABLE 9

COMPARISON OF ACID REMOVAL RATES

	Acid Removal Mechanism		
	Leaching (lb/yr)	Flooding (lb/yr)	Gravity Diffusion (lb/yr)
McDaniels Test Mine	65.7	6.3	31.9
Auger Hole #1	41.2	47.4	11.9
Auger Hole #3	38.4	49.8	1.5
Auger Hole #4	33.9	24.1	3.1
Auger Hole #5	11.1	6.1	2.7
Auger Hole #6	15[illegible].8	26.6	13.7

Leaching removal is the most important mechanism, contributing about 50 per cent of the acid load. Inundation removal is responsible for 20 per cent of the acid, and the remainder is removed by gravity diffusion. As would be expected from the description of the mechanisms, gravity diffusion fluctuated less from year to year than did the leaching and inundation removal rates. The diffusion is independent of the quantity and frequency of precipitation which serves as the driving force for the other mechanisms. The relative uniformity, or lack thereof, may be seen in more detail by examining the sample output for

1970 shown in Appendix C. For all months, gravity diffusion is always two or three pounds while leaching and inundation removal have sharp peaks in the spring. The rest of the year inundation removal virtually ceases, and leaching removal is at about the same level as gravity diffusion with occasional peaks corresponding to rainy periods. Simulation data for other years also show this pattern. There are even greater peaks in the inundation and leaching rates for the very high acid load year, 1968.

SECTION IX

UTILIZATION OF MODEL

Although a model capable of describing past events at a drift mine has been developed, the actual objective of this investigation, namely to make predictions, must still be accomplished. The use of the model of a drift mine for prognosticating falls into two areas; i.e.,

1. prediction of what will happen under different conditions at McDaniels Test Mine, and

2. showing how the model may be generalized for use with other pyritic systems.

PREDICTIONS

The best test of any model is how well it can foretell what will happen when perturbations are imposed on the system in question. For a drift mine, the perturbation of most interest is the exclusion of oxygen from the atmosphere. McDaniels Test Mine has been under a positive pressure of nitrogen for more than two years. The oxygen level in the mined-out volume has been reduced to less than one per cent, and the acid loads from the mine have started to decrease. The question to be answered, or predicted, is how long flow from the mine will remain acidic. The answer is "probably a very long time" if one considers that oxygen dissolved in water will continue to enter the mine. Practically speaking, there is very little oxidation occurring, so the real prediction is how rapidly stored products will be removed.

The product removal rate in the model has been related to the infiltration of water from the surface of the ground. The rate of infiltration in turn is dependent on the level of precipitation. Therefore, a number of predictions are possible depending on the estimate of precipitation. The best source of precipitation data is meteorological records from previous years. During the 1965 - 1970 period, the rainfall in southeastern Ohio ranged from 30 to 45 inches per year. In 1968 there were 45 inches of rain including nearly 13 inches in May. In 1967 and 1969, precipitation totaled only 30 inches. Since the annual average rainfall is about 38 inches in the region, the 30- and 45-inch years probably represent extremes. Therefore, duplicates of 1968 and 1969 will be used as sample data for wet and dry years. The prime reason for using existing rainfall data for generating predictions is to ensure that the natural pattern of storms and dry spells is included. Another reason for using the existing data is that the program requires temperature data, and these are already available in the data decks for preceding years.

Two sets of predictions have been undertaken. The more important one is determining what will happen if the low oxygen level is maintained

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in McDaniels Mine. The second set investigates the effect of imposing changes on the system at different points in the hydrological year. The initial product storage and hydrologic conditions for the predictions were established by allowing the program to run through the normal 1967 - 1970 simulation.

The prediction of what will happen if the current low oxygen level is maintained will be useful in evaluating the nitrogen addition experiment of Smith and Shumate.[37] On the basis of an observed decrease in acid load of 30 per cent during 1970, acid loads should be reaching a very low level within two years. To check this hypothesis, the simulation of two years at McDaniels Mine has been run for cases of above and below average rainfall. These cases bracket the expected precipitation and removal rates and give the range of times that will be required to achieve a desired minimum acid load level.

The results for the two cases are remarkably similar. About 35 pounds of acid removal were predicted for 1971 and about 20 pounds for 1972 in each case. Since the results are identical, only the predictions for the high rainfall case are shown in Fig. 20. The expectation of a substantially higher rate for the wet year was based on the high acid loads in 1968, which included a period when oxygen was being injected into McDaniels Mine.

The breaks in the curve in Fig. 20 indicate periods when the program predicts alkaline drainage from McDaniels Mine. The actual fulfillment of this predictions depend on the validity of the estimate that ground water entering the mine contains 20 ppm alkalinity. Also to be verified at some point in the future is the tacit assumption that no acid is diffusing into or otherwise entering the drainage from outside the stated boundaries of the system. Whether or not the observed drainage ever becomes alkaline at McDaniels Mine, the acid load should be down to 20 or 25 lb/year by 1972. On a concentration basis, this is about 20 ppm acidity in the drainage.

In the second simulation experiment the effects of the timing of changes in the concentration of oxygen in the mine atmosphere were studied. The situation that has been studied assumes that the oxygen level at the McDaniels Mine was returned to 21 per cent as in normal air. Two cases have been examined:

1. The oxygen level was raised on January 1, 1971. In this case the change immediately precedes the wettest part of the year.
2. The oxygen level was raised on July 1, 1971. In this case the change follows the rainy season.

For this experiment, the average rainfall year, 1970, was used as the data source.

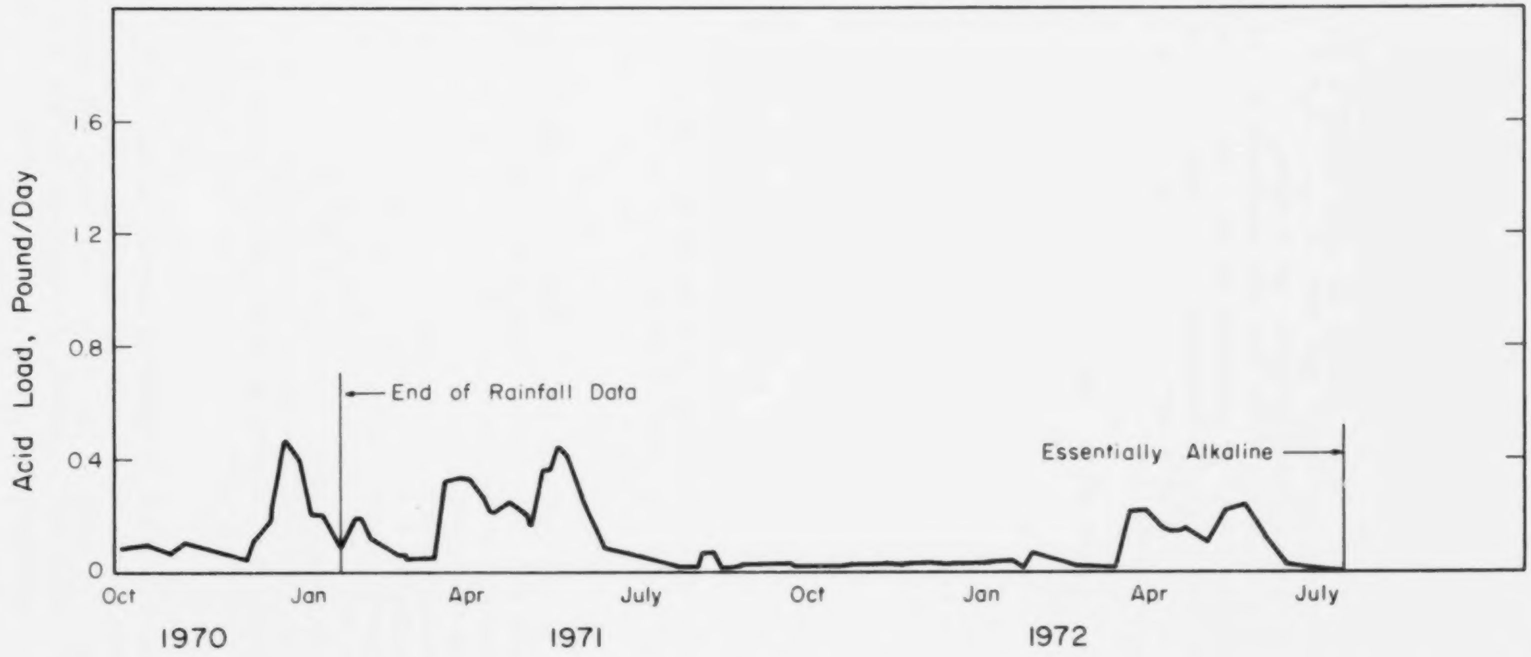

Figure 20 - Acid Load Predictions for 1971 and 1972 Using 1968 Rainfall Data

The results of this experiment are shown in Fig. 21. For Case 1, where the oxygen level was changed in January, there is a rapid system response in terms of increased acid load. The curve plotted for Case 2 during the first half of 1971 represents the acid load if the nitrogen addition had been continued during that period. For Case 2, the response to increased oxygen levels appears more slowly. However, if the Case 2 curve in Fig. 21 is compared with the continued addition curve in Fig. 20, it is apparent that there are slight increases in acid load even when the reintroduction of oxygen into the mine was done during the dry season. Significant increases in acid load for Case 2 do not appear until the wet spell in late December.

In the second year of the simulation, differences in acid load for the two cases become smaller. However, the fact that differences in acid load still exist a year after oxygen was restored to the mine atmosphere can be taken as evidence of the slowness of the time response of the system. This delay in change of drainage composition is in accord with the observations of Smith and Shumate[37] in the natural laboratory study. They had estimated lag times for McDaniels Mine in the range from six months to one year.

The simulation experiments that have been run are examples of tests that can be performed with this model. Other investigations could include the use of zero-order oxidation rate (oxygen concentration independent) or evaluating the effects of "leakages" of oxygen into the mine through the over-burden. The most important use of the model still to be described is the application to other pyritic systems. This topic will be discussed in the following section.

GENERALIZATION OF MODEL

A model has been developed which well describes the flow of acidic mine drainage from a specific drift mine. This model includes physical, chemical, hydrological, and meteorological features of the mine environs. To convert this specific model to a general model of pyritic systems, two levels of generality must be considered. The first level is that of geometric similarity to other drift mines. At this level, our model is virtually a general model. The second level of generality is chemical similarity to any other system containing oxidizable pyrite, such as refuse piles or auger holes. At this level, the spatial configuration is different and limits the use of coordinate based features of the drift mine model, to say nothing of possible mechanistic differences.

Geometric Similarity

The utilization of the model in cases of geometric similarity can be considered in terms of the underlying assumptions and input data requirements for the two parts of the model--oxidation and product removal. The oxidation model requires physical and chemical information about the mine. Physical data include the length of the exposed coal face, the

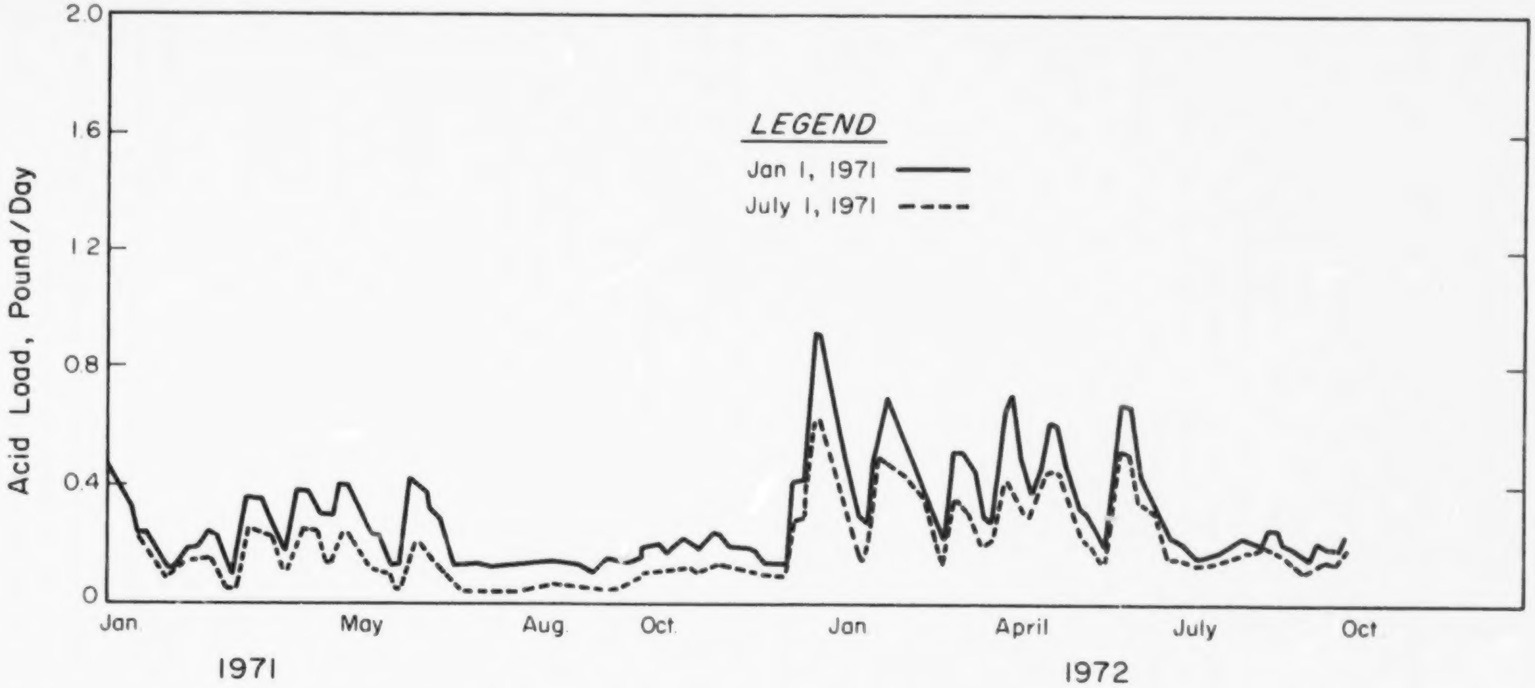

Figure 21 - Effect of Timing of Increase of Oxygen Level on Acid Load Predictions for 1971 and 1972

number and thickness of coal and shale layers in the seam, and the porosity of the pyrite-containing strata. Chemical data include pyrite reactivity and oxygen concentration in the mined-out volume. If the required information is not available, certain approximations can be made. For example, in a mine containing only open rooms, the perimeter of the mine cavity can be used to estimate the length of exposed coal face. If the mine contains pillars or passageways, the surfaces of these must be considered as part of the exposed area. The perimeter of a pillar could be used as a measure of the exposed length, but it must be remembered that the volume-to-surface ratio is lower for a pillar than for a wall. Hence, there will be fewer oxidation products formed per unit area of pillar than for the same area of regular wall. Using the length of exposed coal face is based on the assumption of a uniform atmosphere in the mined-out volume. The computer program has been written to handle varying conditions along the exposed surface (this is the "I" direction), but the time required for computer calculations increases linearly with each increment of change in conditions along the surface.

In the absence of porosity and reactivity data, oxidation rate data of the type that Larez[18] reported may be used. In fact, the computer program for this model has been written under the assumption that such data will be used.

Actual data are required to describe the number and thickness of coal and shale layers in the seam. Finally, there must be an estimate of the bulk oxygen concentration in the mine. Starting with the bulk oxygen level and reactivity data, the oxygen gradients within the strata can be calculated using Eq. (7).

The rate of removal is determined as the sum of the rates of removal by three mechanisms. The usefulness of this part of the model in the general case must be evaluated in terms of the suitability of each mechanism.

The dependence of the gravity diffusion rate on the concentration of stored products is fundamental to the definition of diffusion. The value, DIFFG(J), used for the fraction of products moved daily by gravity diffusion, was chosen on the basis of experimental observation and by correlation of acid loads under low water flow conditions at McDaniels Mine. The fact that two independent evaluation techniques yielding similar values of the gravity diffusion coefficient indicate that the value could have general applicability.

The leaching removal mechanism has been related to the trickling of water downward from the surface after precipitation. The validity of this mechanism in the general case depends largely on the strata overlaying the coal seam. If there is an impervious layer which blocks the percolation, no water is available for leaching. Where there is a highly fractured sandstone overburden, as at McDaniels Mine, percolation is rapid, and leaching is an important removal mechanism. Since there are very few totally impermeable formations, leaching removal will occur in most mines. The overburden will influence the time delay between precipitation and observed changes in the leaching rate. The constants in the model derived from McDaniels data represent a time delay of two to four days depending on the wetness of the soil. For overburden less permeable than fractured sandstone, the time delay will be greater and the observed response will be flatter; that is, there will be no sharp increases in acid load after a storm.

Products can be removed only by inundation if the coal seam lies in the range of movement of the water table. Evaluation of this removal mechanism for different sites requires information about the location of the pyritic material relative to the water table.

In general, the removal rates depend on underground water movement. The calculation of water flow variations in our model is based on fundamental information such as infiltration capacity, potential evapotranspiration, and meteorological data. A number of techniques have been described for determining infiltration capacity.[11] Thornthwaite and Mather[42] have presented a method to estimate potential evapotranspiration if the latitude and vegetative cover are known for the site in question. Monthly summaries of weather data are published by the Environmental Data Service.[9] From the fundamental information, the day-to-day flow variations can be predicted.

Precipitation falling as snow is treated as being delayed until temperatures above freezing occur. The rate at which the snow melts is proportional to the number of degrees above freezing.[44] The melted snow is treated as an equivalent amount of rainfall as far as flow rate calculations are concerned. This way of computing snow melt is based on the assumption that in the McDaniels Mine area, southeastern Ohio, snow melts throughout the winter rather than accumulating to great depth, and then melting in the spring. Depending on the type of winter, other techniques have been described for calculating snow melt runoff rates. However, the actual estimate of water flow is usually obtained by correlation of data for each site.[44]

Finally to use this model, the investigator must obtain an estimate of the "water shed" area of the mine being studied, as described in Appendix E. This value controls the magnitude of flow predictions, but has no influence on the rate of product removal or formation. The area does influence the concentration of acidity in the drainage. The concentration of acid is an important biological consideration.

Summary of Data Requirements

The basic information required to use our oxidation and removal model for another drift mine includes the following items:

1. Prevailing oxygen concentration in mined-out volume
2. Number and thickness of coal and shale layers in seam
3. Rate constants and porosity of each layer
4. Area of air-solid interface
5. Meteorological data
6. "Water shed" area of mine
7. Position of mine relative to water table; or preferably, flow and acid load data during high and low flow periods.

These data can be plugged into the model and calculations made using the procedures described in Appendix E. It is not unreasonable to expect the model to estimate annual acid loads to within ± 15% of the true value when flow and acid load data are available. The monthly predictions would be less reliable on a percentage basis.

Refuse Pile

The following discussion of a refuse pile draws extensively on the work of Good[13] at the New Kathleen pile of Truax-Traer. The oxidation in the refuse pile occurs in a zone about 10 inches thick at the surface of the pile instead of extending as much as 50 feet into the binder as in a coal seam.[35] A clay mantle which blocks oxygen transport is the stated reason for the limited reaction zone. However, the concentration of pyrite is so great in the refuse that it is entirely possible that the oxygen gradient goes to zero in this short distance. If data on the bulk porosity of the refuse and the pyritic content were known, the oxygen gradient could be calculated using the exponential expression, $X_{Co} = X_{Co_0} \exp[-(k_R/D)^{1/2} Z]$, developed for coal and shale binders. However, Good has presented rate information on the basis of pounds of acid formed per day per acre of refuse pile area. On a smaller scale, Brown[5] took samples from the New Kathleen pile and obtained laboratory scale oxidation rates. Since the laboratory conditions are well defined, Brown's data can be used to estimate a rate constant for the exponential gradient calculation. Brown's laboratory rates check Good's field data quite well.

While there is a similarity in the area of oxidation between refuse piles and drift mines, major differences arise in the removal mechanisms. In drift mines, underground water flows are responsible for continuous removal of oxidation products. In refuse piles, oxidation occurs, for the most part, above the level of ground water flows. A fourth removal mechanism, physically impossible underground, becomes dominant. This is the direct washing by precipitation on the refuse pile. This is analogous to the underground leaching by trickling water. The rain water washing mechanism is efficient since the water, uncontaminated by acid, contacts a region of high product concentration, and the resultant acidic solution quickly flows away by gravity. The key point brought out by Good[13] and Corbett[10] is that not all of this acidic solution immediately runs off into receiving streams. Instead, a fraction of from 15 to 30 per cent of the drainage flows into the pile and is temporarily stored. This stored water is gradually released as flow or springs at the base of the pile.

The drainage flow behavior of a refuse pile can be modeled by starting with a material balance, as was done for the drift mine. Similar factors must be considered, including rate and frequency of precipitation, infiltration capacity, temperature, and evaporation. Transpiration will not be very important since the acidic conditions at the surface of a refuse pile are not conducive to plant growth. A storage tank model could be used to describe the head or driving force available for flow from the pile. If a storage tank model were used, the tanks could only be assigned limited volumes. In other words, like a sponge, the pile can only hold so much water. Any additional water runs off immediately. This immediate acid runoff is of major importance since it is the sudden shock of acidity which causes much damage to the receiving stream.

The storage tank concept has physical validity since Good, using test well measurements, observed distinct water storage volumes in the New Kathleen refuse pile. The number and capacity of storage tanks in a model could be determined empirically for a specific pile. This information might be generalized for refuse piles on the basis of a storage volume per unit area of refuse pile. To summarize, Good[13] and Brown[5] have presented sufficient information for the development of a model of drainage flow and acid load from a refuse pile. Such a model could give a very good estimate of the quick runoff and acid release during or immediately after a storm. The daily flows from internal storage could be estimated to within a factor of two or three.

Strip Mine System

Another type of pyrite system geometrically dissimilar to a drift mine is a strip mine. Development of a strip mine model requires an extensive background in hydrology. In this type of mining, the cuts taken and the spoil banks left behind distort natural water flow patterns. The oxidation or acid load can still be estimated by the techniques described in Section VI.

Sternberg and Agnew[40] have undertaken the development of a model of drainage in a surface-mined area. They obtained solutions for changes in ground water elevation and ground water flow that would occur in response to a uniform rate of deep percolation over the spoil bank. The solution for ground water flow can be used to predict maximum and minimum flows from the spoil bank to the last cut.

SECTION X

STATUS OF MODEL DEVELOPMENT

It should be emphasized that the capability of the mathematical model to predict flow and acid load has not been thoroughly explored. For example, there has been no attempt to optimize the value of TANK for the auger holes to obtain a better match of field data. A larger value of TANK would have decreased the fluctuations in predicted flows shown in Figs. 17-21. But rather than optimize by trial-and-error procedures, the value of TANK, calculated as described in Appendix E, was used to test the generality of procedures found to be successful for the McDaniels Mine. It is now apparent that the calculated values of TANK for the auger holes are too small. Better values would have been obtained by assuming TANK numerically equal to that used for the McDaniels Mine (see Table 14, Appendix E).

Alternative forms of an equation for calculating ADD were never checked. For example, it would seem more logical to describe the relationship between ADD and WOVERW by an exponential rather than a linear function. As the soil layer approaches saturation the ADD should increase more rapidly than proportional to WOVERW. Expressing ADD as an exponential function of WOVERW would also result in a more rational relationship as derived from field data, between TANK and HEAD.

The more underground mine systems that are modeled and checked with field data, the more general and reliable the model can be made. Ideally, the constants of the flow and acid load equations can be related to the geologic-hydrologic features of the system in terms of the physical model on which the mathematical model is based. At the present time, however, the reliability of this relationship is not known. Comparison of constants such as presented in Table 14 would be very informative if a wider range of pyritic systems were modeled.

The acid load data for the Decker No. 3 Mine was estimated without using any information on the geology of the area in which the mine is found. The pyrite-bearing zone was assumed to be coal having the same sulfur content and void fraction as the coal found at the McDaniels site. This could account for the relatively poor agreement between predicted and observed acid load data for a mine model which predicted flow data quite well.

On the other hand, the fact that acid loads can be predicted by a model based almost entirely on field data poses the question, "How critical is the location and concentration of pyritic material in the coal and shale strata to the definition of a good model?" If no field data are available, as would be the case if one were to develop a model for a proposed mine site, geologic and hydrologic data must be used to estimate the amount of pyritic material that would be exposed to air (i.e., not submerged) over most of the hydrologic year. The actual effect of

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assuming different strata and pyrite concentrations on acid load prediction was not studied.

SECTION XI

ACKNOWLEDGEMENTS

The majority of the work in translating the conceptual model of an underground pyritic system to a useable calculational mode was performed by Dr. A. H. Morth as part of his Ph.D. dissertation in Chemical Engineering. The subroutine REMOVE included in this report is a modification of Dr. Morth's subroutine. The modification was made by Mr. Kurtis Chow as part of his research toward a Master of Science degree in Chemical Engineering. Professor Edwin E. Smith, Department of Chemical Engineering, was research advisor for both graduate students. Dr. Morth is now with the Ohio Geological Survey.

Professor Harry Hershey, also of the Department of Chemical Engineering, contributed to the writing and debugging of the computer programs. Professor K. S. Shumate, Department of Civil Engineering, provided guidance in the areas of hydrology and geology as well as being responsible for much of the experimental data used in formulating the model.

Detailed data on the Decker No. 3 Mine were furnished by Noel N. Moebs.

SECTION XII

APPENDIXES

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APPENDIX A

GRADIENT COMPUTER PROGRAM

During the investigation of the influence of "breathing" on pyrite oxidation, a complicated differential equation was derived. This second-order, variable-coefficient, unsteady-state equation is shown here again:

$$C \frac{\partial X_{Ox}}{\partial \theta} = CD_{AB} \frac{\partial^2 X_{Ox}}{\partial Z^2} + \frac{\Delta P(\theta)(L-Z)}{RT} \frac{\partial X_{Ox}}{\partial Z} - X_{Ox} \frac{\Delta P(\theta)}{RT} .$$

Since there are no straightforward analytical solutions to this equation, it has been solved using finite difference approximations and digital computation. Crank-Nicolson implicit finite differences have been used to estimate all derivatives. Using the notation "I" for steps in the Z(distance) domain, and "J" for steps in the θ(time) domain, the following approximations are obtained:

$$\frac{\partial X}{\partial Z} = \frac{1}{\Delta Z} [X(I+1, J+1) - X(I, J+1)]$$

and

$$\frac{\partial^2 X}{\partial Z^2} \quad \frac{0.5}{(\Delta Z)^2} [X(I+1, J+1) - 2X(I, J+1) + X(I-1, J+1)$$

$$+ X(I+1, J) - 2X(I,J) + X(I-1,J)] .$$

The next step is the collection of coefficients of each time and distance term. The collection of constants for the equation is shown in Table 10. The six sets of coefficients are general and are equally valid for a point X(M,N). To evaluate an X(I,J) means that the five surrounding X values must be known. However, this evaluation can not be done directly since the J+1 terms are in the next time step. Therefore, it is necessary to solve for all the J+1 terms first, and then back substitute. This may be easily done since the matrix in Table 10 is tridiagonal having nonzero elements only on the main diagonal and on the diagonals immediately above and below the main diagonal. The solution of this matrix is obtained using the "TRIDAG" subroutine of the Ohio State University Chemical Engineering package. To use "TRIDAG," boundary conditions must be known, and a standard setup followed. Since the solution to the matrix is implicit, the (I, J+1) terms are defined as the main diagonal.

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TABLE 10

FINITE DIFFERENCE COEFFICIENT MATRIX

Terms	X(I-1, --)	X(I, --)	X(I+1, --)
X(--, J)	$\frac{0.5\ CD_{AB}}{(\Delta Z)^2}$	$-\frac{CD_{AB}}{(\Delta Z)^2} + \frac{C}{\Delta\theta}$	$\frac{0.5\ CD_{AB}}{(\Delta Z)^2}$
X(--, J+1)	$\frac{0.5\ CD_{AB}}{(\Delta Z)^2}$	$-\frac{CD_{AB}}{(\Delta Z)^2} + \frac{C}{\Delta\theta}$	$\frac{0.5\ CD_{AB}}{(\Delta Z)^2}$
	$+ \frac{\Delta P(L-Z)}{RT}$	$-k_R C + \frac{\Delta P}{RT}$	$- \frac{\Delta P(L-Z)}{RT}$

The setup of "TRIDAG" for our system is as follows:

Boundary Conditions

1. For J = 1, $X(I) = X_O \exp[-(k_R/D)^{1/2} I\Delta Z]$. This is a restatement of the analytical oxygen gradient, a good initial approximation.
2. For J = 1, 2,...N, $X(1) = X_O$. The first concentration increment is the bulk concentration for all time steps.
3. For I = N, where N is much greater than 1, X(N) = X(N+1). In other words, at a great distance from the air-solid interface, the oxygen concentration gradient is zero.

Column Vectors

1. A(N) = coefficients in lower diagonal (I-1, J+1).
2. R(N) = coefficients in main diagonal (I, J+1).
3. C(N) = coefficients in upper diagonal (I+1, J+1).
4. D(N) = coefficients of known values such as X(0,J), X(N,1), X(1,J), and so forth.

The "GRADIENT" program functions by calculating the vectors A, R, C, and D. Once these vectors are evaluated, the subroutine "TRIDAG" is called. "TRIDAG" solves the matrix described by A, R, C, and D and returns the solution vector X(N), the oxygen mole fraction gradient. The program prints the values of X(N) and then repeats the calculations for as many time steps as are desired.

The program includes provision for varying the channel length, L, and for using different size time and distance increments. A printout of the program and samples of the output are shown on the following pages.

GRADIENT Program

MAIN

```
C  THIS PROGRAM ESTIMATES OXYGEN MOLE FRACTION
C     IN A LONG CHANNEL.  CRANK NICOLSON FINITE
C     DIFFERENCE APPROXIMATIONS ARE USED FOR THE
C     DERIVATIVES.  THE RESULTING SERIES OF EQUATIONS
C     ARE SOLVED USING THE 'TRIDAG' SUBROUTINE
C
C  THE EQUATION BEING SOLVED IS
C     C*DX/DT = C*DAB* (D2X/DZ2) - K*X*C + X*DELP/(RT)
C     - DELP/(RT) * (L-Z) * (DX/DZ)
C
        DIMENSION A(1000), R(1000), C(1000), D(1000),
     1 X(1000), XSTORE(100,4), TSUM(100)
C
C  IN IS INPUT UNIT NUMBER
C     THIS IS UNIT NUMBER 5 AT OHIO STATE UNIVERSITY
        IN = 5
C  IO IS OUTPUT UNIT NUMBER
C     THIS IS UNIT NUMBER 6 AT OHIO STATE UNIVERSITY
        IO = 6
        IO = 6
C
C  READ INITIAL CONDITIONS AND OTHER DATA
C  L IS LENGTH OF CHANNEL
C  N IS NUMBER OF INCREMENTS PER FOOT
C  NORDER IS ORDER OF REACTION
C  M AND MIN CONTROL ITERATIONS AND PRINTED OUTPUT
C
        READ(IN,1001)  L, N, M, MIN , NORDER
        NSTORE = NORDER
C
C  DTHETA IS TIME INCREMENT IN HOURS
C  P IS AMBIENT PRESSURE, MM. HG.
C  T IS AMBIENT TEMPERATURE, DEGREES FAHRENHEIT
C  RATEK IS REACTION RATE CONSTANT
C  DAB IS OXYGEN IN AIR DIFFUSIVITY
        READ(IN,1000) DTHETA, P, T, RATEK, DAB
        NL = N*L
C  GAS CONSTANT MM.HG.FT**3 / GM.MOLE DEGREE RANKINE
        E = 760. * 359. / (454. * 492.)
C
        WRITE(IO,2002) DTHETA,E,P,T,RATEK,NORDER,L
        WRITE (IO, 2005)
        ZN = N
C  CALCULATE DELTA Z
        DZ = 1.0 / ZN
C  SAWTOO CAUSES DELTA P TO CHANGE SIGN DAILY
        SAWTOO  = -1.
        NHOURS = 48
        NHRS = NHOURS
        COUNT = 16.0
```

```
C  ASSUME A DAILY DELTA P OF BIGDP MM. HG.
       VOL = 8.33
       BIGDP = 12.
       DELTAP = BIGDP / NHOURS
       NHOURS = NHOURS + 1
C
C  ESTABLISH INITIAL EXPONENTIAL GRADIENT
C
       X( 1) = .21
       ROOT = SQRT ( RATEK / DAB )
       NN = NL + 2
       DO 110  I = 2, NN
       K = I
       Z = DZ * ( I - 1 )
       X( I ) = .21 * (EXP (-ROOT * Z ) )
       IF (X(I) .LT. 1.E-40) GO TO 111
  110  CONTINUE
       GO TO 113
  111  DO 112 I = K, NN
  112  X(I) = 0.0
  113  CONTINUE
   48  CONTINUE
C
C  START A SERIES OF CYCLES
C
       DO 30  MM = 1, M
       SUM = 0.0
       DELTAP  =  DELTAP *  SAWTOO
       TIME = 0.0
C  START A 24 HOUR CYCLE
       DO 47  NTIME  = 1, NHOURS
       P = P + DELTAP
       RHO = 1.34 *(P/ 760.) * (492.0 / 515.0)
       CTOTAL = P/ (E*T)
C  CALCULATE SECOND ORDER CONSTANT
       CON1 = 0.5*CTOTAL*DAB  / (DZ**2)
C  CALCULATE TRANSPORT CONSTANT
       CON2 = DELTAP /(E*T)
C  CALCULATE TIME CONSTANT
       CON3  = CTOTAL / DTHETA
C
C  CALCULATE CONSTANT FOR INFLUENCE OF REACTION ORDER
       CON4 = .21* RATEK * CTOTAL*( 1 - NORDER )
C  CALCULATE TRIDAG COEFFICIENTS
C  A, B, AND C ARE COEFFICIENTS OF UNKNOWN TERMS
C  D IS SOLUTION TERM
       DO 1  I = 1, NL
       C(I)  =  CON1  - CON2*(NL - I)
```

```
      A(I)  =  CCN1  + CON2*(NL - I    )
      IF ( X(I) .LT. 0.02 ) NCRDER  = 1
 1    R(I)  = -2*CON1  +  CON2 - CON3 - RATEK *
     1 CTOTAL * NCRDER
      NORDER = NSTCRF
C   INTEGRATE QUANTITY OF OXYGEN CONSUMED IN CHANNEL
      IF (NORDER .EQ. 1 ) GC TC 301
      DO 300  I = 1, NL
      IF ( X(I) .LT. 0.02 ) NORDER  = 1
      SUM = SUM + 0.21*RATEK*DTHETA * (1-NORDER) *
     1 RHO * DZ
      SUM = SUM + DZ/ 6.0 * (X(I+2) + 4.0 * X(I+1)
     1 + X(I)) * RATEK * DTHETA * NCRDER
 300  CONTINUE
 301  CONTINUE
      NCRDER = NSTCRE
      IF ( NORCER .EQ. 0 ) GO TO 302
      DO  99  I = 1, NL, 2
      SUM = SUM + DZ/ 3.0 * (X(I+2)+4.*X(I+1) +
     1 X(I)) * RATEK * DTHETA * RHO * NCRDER
  99  CONTINUE
 302  CONTINUE
      J =NL- 1
      D(1)  =-CON1* ( X(1) - 2*X(2)  + X(3)) - CON3
     1 *X(2) -(CON1 +CCN2 * (NL-1)) * X(1) + CON4
      DO 4  I =2,J
      IF ( X(I) .LT. 0.02 ) CCN4 = 0.0
      D(I)  = -CON1*(X(I) - 2.*X( I + 1) + X(I +
     1 2)) - CON3 * X(I+1) + CCN4
      NK  =  I + 1
      IF(ABS( D(I)) .GT.  1.E-20)  GO TO 4
      DO 5  LL = I, NL
   5  D(LL) = 0.0
      GC TO 8
   4  CONTINUE
   8  CONTINUE
      D(NL) =  -CCN1 *(X(NL -1) - 2.* X(NL))   -
     1 CON3 * X(NL) + CON4
C   ESCAPE FROM CC LCOP AT END OF 24 HOUR CYCLE
      IF( NTIME .EQ. NHCURS ) GC TC 30
C   PRINT INITIAL AND FINAL SETS OF CONCENTRATION DATA
      IF( MM .EQ. 1 ) GO TO 21
      IF ( MM .LT.  MIN) GC TC 20
  21  CONTINUE
      IF(NTIME - 1 ) 9, 9, 15
C   WRITE OUT EVERY 8TH TIME INCREMENT
  15  FLAG = ( NTIME - 1 ) / COUNT
      NFLAG = FLAG
      FLAG = FLAG - NFLAG
      IF ( ABS (FLAG) .GT.  0.01 )  GO TO 20
   9  WRITE (IC,2000) MM , TIME, P
```

```
C  WRITE OUT FIRST 20 CONCENTRATION INCREMENTS
        DO 10   I = 1, 20
        DIST = DZ *(I - 1 )
        WRITE(IO,2001) DIST,X(I),A(I),R(I),C(I),D(I)
   10   CONTINUE
C  WRITE OUT EVERY FOURTH DISTANCE INCREMENT
        DO 11   I = 21, NK, 4
        DIST = DZ *(I - 1 )
C  PRINT ONLY NON ZERO RESULTS
        IF( X(I) .LE. 0.0001)  GO TO 20
   11   WRITE(IO,2001) DIST,X(I),A(I),R(I),C(I),D(I)
   20   CONTINUE
C  STORE DAILY DATA FOR LATER PRINTOUT
        IF( NTIME .NE. NHRS ) GO TO 80
        XSTORE (MM, 1) = X(2)
        XSTORE (MM, 2) = X(15)
        XSTORE (MM, 3) = X(35)
        XSTORE (MM, 4) = X( 100)
   80   CONTINUE
        CALL TRIDAG( A, R, C, D, X, NK)
C  TRIDAG IS AN OHIO STATE SUBROUTINE FOR SOLVING
C     TRIDIAGONAL MATRICES SUCH AS THOSE ARISING FROM
C     IMPLICIT SOLUTIONS OF MASS TRANSPORT EQUATIONS
        DO 150  I = 1, NN
        IF( X(I) .LT. 0.0 ) X(I) = 0.0
  150   CONTINUE
        TIME = TIME + DTHETA
        TSUM(MM) = SUM * 120.  / 112. * VOL
   47   CONTINUE
   30   CONTINUE
        WRITE(6, 2003)
        DO 31  MM = 1, M
   31   WRITE (IO,2004) MM, XSTORE(MM, 1), XSTORE(MM,
       1 2), XSTORE(MM,3), XSTORE(MM,4), TSUM(MM)
        STOP
 1000   FORMAT( 5F10.6)
 1001   FORMAT( 5I5)
 2000   FORMAT(////  '  THIS IS DAY ',I5, '  AFTER  ',
       2 F8.3, '  HOURS', // 12X, ' THE PRESSURE IS  ',
       2 F7.3, '  MMHG.' , ///15X, 'DEPTH', 10X,
       3 'O2 FRACTION', 8X, 'A(I)',15X,'R(I)', 13X,
       4 'C(I)',  15X,  'D(I)')
 2001   FORMAT(1HO,10X, F10.3, 10X, F 10.6, 4E17.8)
 2002   FORMAT(1H1, 'DT  =',F4.2, '  HR.' // ' GAS ',
       1 'CONSTANT  =', F6.4,// ' INITIAL PRESSURE  =',
       2 F6.1, '  MM.HG.', // ' TEMPERATURE  =',F6.0,
       3 '  DEGREES R.',// ' RATE CONSTANT =', F10.8,//
       4 ' ORDER OF REACTION IS ', I2,//' LENGTH  IS',
       5 I3, '  FEET' )
```

```
2003   FORMAT ( 1H1, '  X(I) VALUES ARE TABULATED ',
      1 'BELOW FOR THE LAST',// ' DAILY TIME INCREM',
      2 'ENT  AT THE 2ND, 13TH, 35TH, AND 100TH ',
      3 'DISTANCE  INCREMENTS', // ' A FORM OF STEADY',
      4 ' STATE IS REACHED WHEN VALUES FOR ALTERNATE',
      5 ' DAYS ARE THE SAME', //' THIS IS USUALLY ',
      6'OCCURS AFTER 20 TO 30 DAYS ',// ' THE FINAL ',
      7 'COLUMN IS THE PYRITE OXIDIZED IN MGMS/DAY',
      7 ///15X, 'DAY',6X,'O2 FRACTION',60X,'OXIDATION')
2004   FORMAT  (16X, I3, 5( 8X, F9.6))
2005   FORMAT ( 1H1)
       END
```

X(I) VALUES ARE TABULATED BELOW FOR THE LAST DAILY TIME INCREMENT AT THE 2ND AND 15TH DISTANCE INCREMENTS. A FORM OF STEADY STATE IS REACHED WHEN VALUES FOR ALTERNATE DAYS ARE THE SAME. THIS USUALLY OCCURS AFTER 15 TO 20 DAYS. THE FINAL COLUMN IS THE PYRTIE OXIDATION IN MILLIGRAMS OXYGEN CONSUMED PER DAY

TABLE 11

DAY	OXYGEN MOLE FRACTION		OXIDATION
1	0.113937	0.002585	9.899684
2	0.185306	0.007099	12.941030
3	0.113768	0.001857	9.487527
4	0.185298	0.007087	12.830996
5	0.113781	0.001784	9.475357
6	0.185298	0.007075	12.825077
7	0.113779	0.001774	9.472585
8	0.185298	0.007072	12.823798
9	0.113779	0.001772	9.471957
10	0.185298	0.007071	12.823528
11	0.113779	0.001771	9.471822
12	0.185298	0.007071	12.823472
13	0.113779	0.001771	9.471774
14	0.185298	0.007071	12.823464
15	0.113779	0.001771	9.471774
16	0.185298	0.007071	12.823457
17	0.113779	0.001771	9.471774
18	0.185298	0.007071	12.823457
19	0.113779	0.001771	9.471774
20	0.185298	0.007071	12.823457

DT = 0.50 HOUR
GAS CONSTANT = 1.2215
INITIAL PRESSURE = 745.0 MM HG
TEMPERATURE = 515. DEGREES RANKINE
RATE CONSTANT = 0.0300
ORDER OF REACTION IS 0
LENGTH IS .400 FEET

```
THIS IS DAY      1 . AFTER      8.000  HOURS
------------------------------------------------------------
              THE PRESSURE IS  740.750  MMHG.
------------------------------------------------------------

------------------------------------------------------------
               DEPTH            O2 FRACTION
------------------------------------------------------------
               0.0               0.210000
------------------------------------------------------------
               1.000             0.131294
------------------------------------------------------------
               2.000             0.082267
------------------------------------------------------------
               3.000             0.050897
------------------------------------------------------------
               4.000             0.030540
------------------------------------------------------------
               5.000             0.017995
------------------------------------------------------------
               6.000             0.012162
------------------------------------------------------------
               7.000             0.012830
------------------------------------------------------------
               8.000             0.012316
------------------------------------------------------------
               9.000             0.011611
------------------------------------------------------------
              10.000             0.010808
------------------------------------------------------------
              11.000             0.009877
------------------------------------------------------------
              12.000             0.008842
------------------------------------------------------------
              13.000             0.007755
------------------------------------------------------------
              14.000             0.006675
------------------------------------------------------------
              15.000             0.005651
------------------------------------------------------------
              16.000             0.004721
------------------------------------------------------------
              17.000             0.003904
------------------------------------------------------------
              18.000             0.003205
------------------------------------------------------------
              19.000             0.002620
------------------------------------------------------------
              20.000             0.002135
```

APPENDIX B

ESTIMATION OF POTENTIAL EVAPOTRANSPIRATION

The use of the Thornthwaite and Mather[42] method for estimation of potential evapotranspiration (PE) requires monthly average temperatures and the latitude for the site. Information on the type of soil and vegetative cover in the region are also required. The PE technique was developed by an analysis of data from all over the United States. The correlations which were developed have been published in the form of a manual of tables.

The best way to use the PE tables is to construct a table of data as they are read. The data shown in Table 12 are listed in six columns.

TABLE 12

ESTIMATION OF POTENTIAL EVAPOTRANSPIRATION

Month	T_{mean} (°F)	Calculation Constants* A	B	C	Inches Potential Evapotranspiration
January	33.5	0.06	0.0	25.4	0.0
February	34.7	0.16	0.0	25.1	0.0
March	42.1	1.19	0.02	30.9	0.62
April	53.3	3.68	0.06	33.3	2.00
May	62.8	6.44	0.10	37.0	3.70
June	71.4	9.34	0.14	37.3	5.22
July	74.7	10.56	0.15	37.9	5.69
August	73.3	10.04	0.15	35.5	5.34
September	66.9	7.78	0.12	31.2	3.74
October	55.6	4.30	0.07	28.8	2.02
November	43.3	1.41	0.03	25.2	0.75
December	34.2	0.11	0.0	24.8	0.0

* Calculation constants are explained in the following paragraphs.

The first two columns in Table 12 contain the name of the month and the monthly average temperature in degrees Fahrenheit. The second, third, and fourth columns contain calculational constants. The significance of these columns, labeled A, B, and C, is as follows:

Column A--Intensity of incident sunlight. This is a function of the temperature and is read from Table 1 in Section I of the PE manual. In physical terms, this variable is an estimate of the energy available to evaporate water.

Column B--Daily unadjusted PE. This term is read from Table 3 in Section II of the manual. It is a function of the sunlight intensity, type of soil, and vegetation.

Column C--Correction factor to convert daily unadjusted PE to monthly values. This factor is based on the latitude and represents the number of 12-hour days of sunlight per month. The correction is based on the fact that plant growth, and transpiration, require sunlight. This term is obtained from Table 6 in Section III of the manual.

The sixth column is the adjusted PE in units of inches of water per month. This value is obtained by multiplying Columns B and C. The values in the sixth column are those which are used in any further calculations. These are the values which have been read into the "PEVAP" subroutine as data.

Thronthwaite and Mather have also presented tables for scaling down the potential evapotranspiration for cases where the soil is less than saturated, as is the assumption in the initial calculation. These scaling factors have been written into the "PEVAP" subroutine.

APPENDIX C

DRIFT MINE PROGRAMMING

and

SAMPLE OUTPUT FOR 1970

OF AUGER HOLE NO. 1

MAIN Program

```
C**
C     THIS IS THE MAIN PROGRAM FOR THE CALCULATION OF ACID MINE
C        DRAINAGE FROM DRIFT MINES.  THE STRUCTURE OF THE PROGRAM IS
C        BASED ON THE MATHEMATICAL MODEL BY MORTH.  THE MCDANIELS
C        RESEARCH COMPLEX WHICH IS ADMINISTERED BY THE OHIO STATE
C        UNIVERSITY HAVE BEEN USED TO DEVELOP THIS MODEL.
C**
C     ESTABLISH ARRAYS FOR THE SYSTEM:
C     THE SYSTEM CAN BE SUBDIVIDED INTO 5 SECTIONS IN I-DIRECTION, 15
C        LAYERS IN J-DIRECTION, AND 30 INCREMENTS IN K-DIRECTION.
C**
      DIMENSION ALT(5,15), DT(5), DIFFG(5,15), PYCON(5,15), RATEK(5,15),
     1REACT(5,15), ROCK(5,15), STORE(5,15,30), THICK(5,15), TOP(5),
     2TYPE(5,15), WASH(5,15), WATER(5,30)
C**
      REAL BLANK, END, YEAR, JAN, FEB, MAR, APR, MAY, JUNE, JULY, AUG,
     1SEPT, OCT, NOV, DEC
C**
      INTEGER CONTOL
C**
      COMMON/CA/ BLANK, END, YEAR, JAN, FEB, MAR, APR, MAY, JUNE, JULY,
     1AUG, SEPT, OCT, NOV, DEC
C**
      COMMON/CB/ ADD, AFLAG, AG, AGO, AMONTH, CONTOL, FLAG, IDAY, KEEP,
     1LAST, LTHETA, PWATER, PWHC, RAIN, RSUM, RSUMA, RTIME, TANK,
     2TMEAN, WSHED
C**
      COMMON/CC/ VAP (12)
C**
C     OPERATIONAL CONSTANTS:
C     IN IS INPUT CHANNEL. AT OHIO STATE UNIVERSITY, IN IS UNIT 5.
C     IO IS PRINTED OUTPUT CHANNEL. IT IS EQUAL TO 6.

C     IP IS PUNCHED OUTPUT CHANNEL. IT IS EQUAL TO 7.
C**
      IN = 5
      IO = 6
      IP = 7
C**
C     INITIALIZATION:
C     AG AND AGO ARE IDENTIFICATION OF THE MONTH BEING EXECUTED.
C     IY IS IDENTIFICATION OF YEAR.
C**
      AGO = BLANK
      AG = BLANK
      IY = 0
```

Preceding page blank

```
C**
C     ESTABLISH CONTROLLING DEVICE FOR THE PROGRAM:
C     IF CONTOL IS EQUAL TO 1, ONLY ADD IS CALCULATED (STATEMENT #100).
C     IF CONTOL IS EQUAL TO 2, ADD, AND TANK ARE CALCULATED (STATEMENT
C        #200).
C     IF CONTOL IS EQUAL TO 3, ADD, FLOW, AND ACID LOAD ARE CALCULATED
C        (STATEMENT #300).
C**
      READ (IN, 5100) CONTOL
  100 CONTINUE
C**
C     CONTOL = 1
C     READ IN DATA FOR CALCULATING ADD:
C     PWATER IS CURRENT WATER STORAGE IN ROOT STRUCTURE IN INCHES.
C     PWHC IS PROVISIONAL WATER HOLDING CAPACITY IN INCHES.
C     VAP IS MONTHLY POTENTIAL EVAPOTRANSPIRATION VALUES.
C**
      READ (IN, 5110) PWATER, PWHC
      READ (IN, 5120) (VAP (I), I = 1,12)
      WRITE (IO, 6380)
C**
C     IF ONLY ADD IS DESIRED, SKIP THE FOLLOWING, AND CALCULATE DAILY
C        ADD (STATEMENT #400).
C**
      IF (CONTOL .LE. 1)GO TO 400
  200 CONTINUE
C**
C     CONTOL = 2
C     READ IN DATA FOR CALCULATING TANK:
C     WSHED IS WATERSHED AREA OF MINE.
C     TANK IS AQUIFER STORAGE OF WATER
C     CONFH IS CONSTANT RELATING AUGIFER STORAGE AND FLOW.
C**
      READ (IN, 5210) WSHED, TANK, CONFH
      WRITE (IO, 6381)
      IF (CONTOL .LE. 2) GO TO 400
  300 CONTINUE
C**
C     CONTOL = 3
C     READ IN DATA FOR CALCULATING ACID LOAD:
C     NFEET IS NUMBER OF AIR-SOLID INTERFACE INCREMENTS
C     NLAYER IS NUMBER OF LAYERS IN COAL SEAM MODEL
C     NDEPTH IS NUMBER OF DEPTH INCREMENTS IN MODEL
C     NPUNCH IS PUNCHED OUTPUT CONTROL
C     DK IS LENGTH OF DEPTH INCERMENTS
C     ALKALI IS GROUND WATER ALKALINITY. IT HAS A VALUE EQUAL TO 20 IN
C        THIS MODEL.
C     FLOWMI IS MINIMUM FLOW TO CAUSE ACID REMOVAL BY FLOODING.
C     HEADMI IS MINIMUM FLOW TO CAUSE ACID REMOVAL BY LEACHING.
C     PER IS A CONSTANT VALUE TO DETERMINE THE DISTANCE THAT IS
C        INUNDATED.
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C     WSLOPE IS HYPOTHETICAL SLOPE OF WATER TABLE.
C     DI IS LENGTH OF AIR-SOLID INTERFACE INCREMENTS
C     TOP IS DATUM PLANE FOR TOP OF COAL SEAM
C     ROCK AND TYPE ARE LITERAL DESCRIPTION OF STRATA
C     ALT IS ELEVATION OF STRATUM RELATIVE TO DATUM PLANE
C     REACT IS OXYGEN CONSUMPTION RATE OF PYRITE.  IT HAS VALUES EQUAL
C        TO 0.5 FOR COAL AND 2.5 FOR SHALE.
C     PYCON IS VOID FRACTION OF THE STRATUM
C**
      READ (IN, 5310) NFEET, NLAYER, NDEPTH, NPUNCH
      READ (IN, 5320) DK, ALKALI, FLOWMI, HEADMI, PER, WSLOPE
      DO 1119 I = 1, NFEET
      READ (IN, 5330) DI (I), TOP (I)
      DO 1200 J = 1, NLAYER
      READ (IN, 5340) ROCK (I,J), TYPE (I,J), ALT (I,J), REACT (I,J),
     1PYCON (I,J)
 1200 CONTINUE
 1119 CONTINUE
C**
C     INITIALIZATION:
C     DIFFG IS GRAVITY DIFFUSION RATE CONSTANT FOR A LAYER
C     STORE IS OXIDATION PRODUCT STORAGE ARRAYS
C**
      NL = NLAYER + 1
      DO 1118 I = 1, NFEET
      DIFFG (I,NL) = 0.0
      ALT (I, NL) = TOP (I)
      DO 1117 K = 1, NDEPTH
      STORE (I, NL, K) = 0.0
 1117 CONTINUE
 1118 CONTINUE
C**
C     CALCULATE RATE CONSTANT (THEORY BASED ON THE MODEL BY MORTH(6))
C     TEMP IS MINE TEMPERATURE CORRECTION FACTOR
C     FTGMOL IS VOLUME OCCUPIED BY GM. MOLE GAS
C     CCPRFT IS CONSTANT FOR CALCULATING RATE CONSTANT
C     CONA IS CONSTANT FOR CALCULATING RATE CONSTANT
C     RATEK IS REACTION RATE CONSTANTS OF STRATA
C     THICK IS THICKNESS OF STRATA
C     DIFFG IS GRAVITY DIFFUSION RATE CONSTANT FOR A LAYER.
C     DIF IS BASE GRAVITY DIFFUSION CONSTANT.
C**
      TEMP = 0.15
      FTGMOL = 359. / 454.
      CCPRFT = (2.54 ** 3) * 1725.
      CONA = CCPRFT * FTGMOL / (0.21 * 32.) * TEMP
      DIF = 0.01
      WRITE (IO, 6300)
      DO 1203 I = 1, NFEET
      DO 1202 J = 1, NLAYER
      REACT (I,J) = REACT (I,J) * 1.E-6 * 24.
      RATEK (I,J) = REACT (I,J) * CONA / PYCON (I,J)
      THICK (I,J) = ALT (I, J+1) - ALT (I,J)
      DIFFG (I,J) = DIF * RATEK (I,J)
C**
C     ECHO INPUT DATA:
C**
      WRITE (IO, 6301) I, J, ROCK (I,J), TYPE (I,J), ALT (I,J),
     1RATE (I,J), PYCON (I,J)
 1202 CONTINUE
 1203 CONTINUE
C**
C     INITIALIZATION:
C     P IS PRESSURE IN MINE
C     DIFF IS GAS DIFFUSIVITY IN SQUARE FEET PER DAY
C     GASC IS GAS CONCENTRATION UNDER MINE CONDITIONS
C     DTHETA IS TIME INCREMENT LENGTH
C     SOX IS TOTAL INITIAL ACID STORAGE
C     WASH IS EQUILIBRIUM PRODUCT STORAGE IN LAYER
C     FRAC IS FRACTION OF STORED PRODUCTS REMOVED DAILY DURING FLOODING.
C**
      P = 454.
      DIFF = 0.692 * 24. * 0.6
      GASC = 32. / 359. * 492. / 515.
      DTHETA = 1.0
      SOX = 0.0
      FRAC = 0.02
      DO 1205 I = 1, NFEET
      DO 1205 J = 1, NLAYER
      READ (IN, 7000) (STORE (I,J,K), K = 1, NDEPTH)
 1205 CONTINUE
      DO 1500 I = 1, NFEET
      DO 1498 J = 1, NLAYER
      DO 1496 K = 1, NDEPTH
      SOX = SOX + STORE (I,J,K)
 1496 CONTINUE
      WRITE (IO, 6305) (STORE (I,J,K), K = 1, NDEPTH)
      WASH (I,J) = STORE (I,J,1)
 1498 CONTINUE
 1500 CONTINUE
      WRITE (IO, 6302) SOX
 400  CONTINUE
C**
C     INITIALIZATION:
C     KEEP IS LENGTH OF MONTH
C     LTHETA IS DAYS SINCE PRECEDING DATA INPUT
C     KAT IS CONTROL DEVICE IN PROGRAMMING
C     RSUM IS MONTHLY ACCUMULATION OF WATER ENTERING STORAGE
C     RSUMA IS ANNUAL ACCUMULATION OF WATER ENTERING STORAGE
C     TSUM ISACCUMULATION OF TOTAL ACID LOAD.
C     WSUM IS TOTAL ACID REMOVED BY LEACHING.
C     FLSUM IS TOTAL ACID REMOVAL BY FLOODING.
C     GSUM IS MONTHLY TOTAL ACID REMOVAL BY GRAVITY DIFFUSION.
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C     YSUM IS MONTHLY ACCUMULATION OF ACID LOAD.
C     YSUMA IS ANNUAL ACCUMULATION OF ACID LOAD.
C     FSUM IS ACCUMULATION OF FLOW PER MONTH.
C     FSUMA IS ANNUAL ACCUMULATION OF FLOW.
C**
      KEEP = 30
      LTHETA = 1
      KAT = 0
 1606 CONTINUE
      RSUM = 0.0
      RSUMA = 0.0
      IF (CONTOL .NE. 3) GO TO 1501
      TSUM = 0.0
      WSUM = 0.0
      FLSUM = 0.0
      GSUM = 0.0
      YSUM = 0.0
      YSUMA = 0.0
      FSUM = 0.0
      FSUMA = 0.0
 1501 CONTINUE
C**
C     READ IN DAILY WEATHER DATA.  THERE IS NO.LIMIT ON THE NUMBER OF
C        YEARS BEING MONITORED, BUT LESS THAN 366 DATA POINTS IN A
C        YEAR IS REQUIRED.
C     AMONTH IS MONTH
C     IDAY IS DATE
C     RAIN IS PRECIPITATION.  ONLY IN THE FORM OF RAINFALL IS PRINTED
C        IN THE OUTPUT.
C     RTIME IS DURATION OF RAINFALL
C     TMEAN IS AVERAGE DAILY TEMPERATURE.
C     OXY IS OXYGEN CONCENTRATION.  IF ACID LOAD IS NOT CALCULATED,
C        LEAVE COLUMN 40-50 EMPTY.
C     IYEAR IS YEAR
C**
      DO 2500 L = 1, 366
      READ (IN, 5130) AMONTH, IDAY, RAIN, RTIME, TMEAN, OXY, IYEAR
C**
C     IF OXY IS A CONSTANT VALUE SUCH AS THE AUGER HOLES, INSERT THE
C        FOLLOWING CARD HERE: OXX = 0.2'
C**
C     ESCAPE FROM PROGRAM AT THE END OF DATA SET BY GOING TO STATEMENT
C        # 2200.
C     PRINT OUT ANNUAL RESULTS BY GOING TO STATEMENT # 3050.
C**
      IF (AMONTH - END) 2250, 2200, 2250
 2250 CONTINUE
      IF (AMONTH - IYEAR) 2255, 3050, 2255
 2255 CONTINUE
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C**
C     CALL SUBROUTINE DAYS TO DETERMINE THE DATE BEING EXECUTED.
C**
      CALL DAYS
C**
C     INITIALIZATION:
C     RKEEP IS VARIABLE TO STAND FOR RAIN.
C**
      RKEEP = RAIN
      RAIN = 0.0
C     PERFORM THE FOLLOWING CALCULATIONS BASED ON THE INFORMATION
C        BETWEEN THE LAST AND THE NEXT INPUT WEATHER DATA
C**
      DO 3005 M = 1, LTHETA
      IF (M .EQ. LTHETA) RAIN = RKEEP
      IF (KAT .NE. 0) GO TO 2305
C**
C     CALL WATBAL TO CALCULATE ADD, TANK, OR FLOW AS INDICATED BY
C        CONTOL.
C     WATBA IS USED TO INITIALIZE VALUES USED IN SUBROUTINE WATBAL.
C        AFTER INITIALIZATION, PERFORM CALCULATIONS FOR THE NEXT DAY.
C**
      CALL WATBA (DSLV, FLOW, M)
      GO TO 3005
 2305 CALL WATBAL (DSLV, FLOW, M)
C**
C     IF ONLY ADD IS DESIRED (CONTOL = 1), PRINT OUT THE RESULTS
C**
      IF (CONTOL .NE. 1) GO TO 500
      IF (AG - AGO ) 1020, 1010, 1020
 1010 WRITE (IO, 6100) AGO, IDAY, RAIN, ADD
      GO TO 1100
 1020 IF (IDAY .GT. KEEP) GO TO 1030
 1025 WRITE (IO, 6100) AG, IDAY, RAIN, ADD
      GO TO 1100
 1030 IDAY = IDAY - KEEP
      WRITE (IO, 6100) AGO, IDAY, RAIN, ADD
 1100 CONTINUE
      IF (IDAY .NE. KEEP) GO TO 3005
      WRITE (IO, 6110) RSUM
      WRITE (IO, 6380)
      RSUM = 0.0
      GO TO 3005
 500  CONTINUE
      IF (CONTOL .GT. 2) GO TO 600
C**
C     IF TANK IS DESIRED (CONTOL = 2), PROCEED WITH THE FOLLOWING:
C     INITIALIZATION AND PRINT OUT RESULTS:
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C**
      IF (AG - AGO) 2020, 2010, 2020
 2010 WRITE (IO, 6200) AGO, IDAY, TANK
      GO TO 2100
 2020 IF (IDAY .GT. KEEP) GO TO 2030
 2025 WRITE (IO, 6200) AG, IDAY, TANK
      GO TO 2100
 2030 IDAY = IDAY - KEEP
      WRITE (IO, 6200) AGO, IDAY, TANK
 2100 CONTINUE
      GO TO 3005
 600  CONTINUE
C**
C     IF FLOW AND ACID LOAD ARE DESIRED, PROCEED WITH THE FOLLOWING:
C     FROM WATBAL, FLOW OF A CERTAIN DAY HAS BEEN OBTAINED.
C     DETERMINE POSITION OF WATER TABLE BY RELATING FLOW TO THE
C        INCREMENTS IN K-DIRECTION WHICH IS INUNDATED.
C     DEHK IS THE DISTANCE IN K-DIRECTION THAT IS INUNDATED. SEE
C        CHAPTER V FOR ESTABLISHING THE RELATION.
C**
      IF (FLOW .LT. FLOWMI) GO TO 3114
      DEHK = PER * SQRT (FLOW - FLOWMI)
      GO TO 3115
 3114 DEHK = 0.0
 3115 CONTINUE
C**
C     XMAX IS TOTAL DISTANCE IN K-DIRECTION
C     XMIN IS DISTANCE IN K-DIRECTION THAT IS NOT INUNDATED.
C**
      XMAX = NDEPTH * DK
      XMIN = XMAX - DEHK
      IF (XMIN) 3307, 3307, 3317
C**
C     WATER IS WATER LEVEL RELATIVE TO THE STRATA.
C**
 3307 CONTINUE
      DO 3311 I = 1, NFEET
      WATER (I,1) = ABS (XMIN) * WSLOPE + ALT (1,1)
      KB = 2
      DO 3315 KA = KB, NDEPTH
      WATER (I, KA) = WATER (I, KA-1) + WSLOPE * DK
      IF (WATER (I,KA) .GT. TOP (I)) WATER (I,KA) = TOP (I)
 3315 CONTINUE
 3311 CONTINUE
      GO TO 3316
 3317 CONTINUE
      DO 3312 I = 1, NFEET
      IF (I .GT. 1) XMIN = XMIN + (ALT (I,1) - ALT (1,1)) / WSLOPE
      DO 3310 KA = 1, NDEPTH
      DF = KA * DK
      KB = KA
      IF (XMIN .LT. DF .AND. KA .EQ. 1) GO TO 3309
      IF (DF - XMIN) 3309, 3309, 3308
 3309 CONTINUE
      WATER (I,KA) = ALT (I,1)
 3310 CONTINUE
      GO TO 3312
 3308 CONTINUE
      DO 3318 KKA = KA, NDEPTH
      WATER (I, KKA) = WATER (I, KKA-1) + WSLOPE * DK
      IF (WATER (I, KKA) .GT. TOP (I)) WATER (I,KKA) = TOP (I)
 3318 CONTINUE
 3312 CONTINUE
 3316 CONTINUE
C**
C     INITIALIZE DAILY TOTAL ACID OUTPUT (TACID).
C**
      TACID = 0.0
C**
C     CALCULATE THE VOLUME OF EACH BLOCK (DVOL).
C     COMPARE ACID STORAGE WITH EQUILIBRIUM ACID STORAGE (WASH)
C     FOR GENERATING ACID STORAGE, FJ = 1 CAN BE USED IN PLACE OF FJ =
C        STORE (I,J,1) / WASH (I,J). FJ IS RATIO OF STORED PRODUCTS TO
C        EQUILIBRIUM STORAGE LEVEL.
C**
      DO 3000 I = 1, NFEET
      DO 3995 J = 1, NLAYER
      DVOL = THICK (I,J) * DI (I) * DK
      FJ = STORE (I,J,1) / WASH (I,J)
      IF (FJ .GT. 1.1) FJ = 1.
C**
C     CALCULATE OXYGEN GRADIENT IN EACH LAYER (SEE REFERENCE 6)
C**
      DO 3990 K = 1, NDEPTH
      TNN = K
      DNK = (TNN - 0.5) * DK
      XNN = OXX * EXP (-SQRT (RATEK (I,J) / DIFF) * DNK)
C**
C     THE FOLLOWING CALCULATIONS DESCRIBE EACH EVENT PROBABLE IN THE
C        BLOCKS
C     UNIFORM MINE STRUCTURE IN K-DIRECTION IS ASSUMED
C     BY COMPARING THE WATER LEVEL TO THE HEIGHT (HITE) WITH RESPECT TO
C        THE DATUM PLANE, WHETHER THE BLOCK IS INUNDATED CAN BE
C        DETERMINED.
C**
      HITE = ALT (I,J)
      IF (HITE - WATER (I,K)) 3648, 3655, 3655
 3648 CONTINUE
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C**
C     IF THE BLOCK IS FLOODED, FOLLOWING EVENTS OCCUR.
C     ALEFT IS PRODUCT STORAGE AFTER FLOODING
C     DTHETA IS TIME INCREMENT LENGTH IN DAYS
C     FLOOD IS ACID REMOVED DURING INUNDATION.
C**
      ALEFT = STORE (I,J,K) * (1. - FRAC) ** DTHETA
      FLOOD = STORE (I,J,K) - ALEFT
      AOUT = FLOOD
      STORE (I,J,K) = STORE (I,J,K) - FLOOD
C**
C     MAINTAIN RUNNING TOTAL OF REMOVAL BY INUNDATION
C**
      FLSUM = FLSUM + FLOOD * 196. / 112.
      IF (FLSUM .LT. 1.E-10) FLSUM = 0.0
      GO TO 3989
 3655 CONTINUE
C**
C     IF THE BLOCK IS NOT FLOODED, OXIDATION OCCURS AND ACID REMOVAL
C        BY LEACHING, AND GRAVITY DIFFUSION DOMINATED.
C     OXIDN IS OXIDATION IN A VOLUME
C     GASC IS GAS CONCENTRATION UNDER MINE CONDITIONS
C     GRAVOT IS GRAVITY DIFFUSION OUT OF A VOLUME
C     GRAVIN IS GRAVITY DIFFUSION INTO A VOLUME
C**
      OXIDN = RATEK (I,J) * GASC * XNN * DVOL * PYCON (I,J) * DTHETA
      GRAVOT = DIFFG (I,J) * STORE (I,J,K) * DTHETA * FJ
      GRAVIN = DIFFG (I,J+1) * STORE (I,J+1,K) * DTHETA * FJ
C**
C     AOUT IS DAILY ACID REMOVAL BY LEACHING.
C     THE NEW ACID STORAGE IN A BLOCK IS THE SUMMATION OF NEWLY
C        OXIDIZED MATERIAL AND THE ACID REMOVED BY FLOODING, LEACHING,
C        AND GRAVITY DIFFUSION.
C**
      AOUT = STORE (I,J,K) * DSLV * FJ
      STORE (I,J,K) = STORE (I,J,K) + OXDIN + GRAVIN - GRAVOT - AOUT
C**
C     KEEP RUNNING TOTAL OF ACID REMOVAL BY LEACHING
C**
      WSUM = WSUM + AOUT * 196. /112.
C**
C     DETERMINE ACID LOAD IN THE BOTTOM LAYER OF THE SYSTEM WHICH
C        WILL BE REMOVED BY GRAVITY DIFFUSION.
C     UP IS DIFFERENCE IN HEIGHT BETWEEN LAYER AND WATER LEVEL
C**
      UP = HITE - WATER (I,K)
      IF (J .GT. 1) GO TO 3989
      IF (UP .GT. 0.) GO TO 3989
      AOUT = AOUT + GRAVOT
C**
C     KEEP RUNNING TOTAL OF REMOVAL BY GRAVITY DIFFUSION
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C**
      GSUM = GSUM + GRAVOT * 196. / 112.
 3989 CONTINUE
C**
C     TOTAL DAILY ACID REMOVAL
C**
      TACID = TACID + AOUT
 3990 CONTINUE
 3995 CONTINUE
 3000 CONTINUE
C**
C     CONVERT ACID LOAD FROM AN OXYGEN CONSUMPTION BASIS TO EQUIVALENT
C        ALKALINITY BASIS.
C     ALK IS FACTOR CONVERTING ACID LOAD FROM OXYGEN CONSUMPTION BASIS
C        TO EQUIVALENT ALKALINITY BASIS.
C**
      ALK = FLOW * ALKALI * 8.33E-6
      TACID = TACID * 196. / 112. - ALK
      TSUM = TSUM + TACID
      TACID = TSUM / 5.
      TSUM = TSUM - TACID
      FSUM = FSUM + FLOW
      FSUMA = FSUMA + FLOW
      YSUM = YSUM + TACID
      YSUMA = YSUMA + TACID
      IDAY = LAST + M
C**
C     PRINT OUT SUMMARY OF DAILY RESULTS
C**
      IF (AG - AGO) 3020, 3010, 3020
 3010 WRITE (IO, 6350) AGO, IDAY, FLOW, TACID, RAIN
      GO TO 3001
 3020 IF (IDAY .GT. KEEP) GO TO 3030
      WRITE (IO, 6350) AG, IDAY, FLOW, TACID, RAIN
      GO TO 3001
 3030 IDAY = IDAY - KEEP
      WRITE (IO, 6350) AGO, IDAY, FLOW, TACID, RAIN
 3001 CONTINUE
      IF (IDAY .NE. KEEP) GO TO 3005
      WRITE (IO, 6341) FSUM, YSUM, RSUM
      WRITE (IO, 6345) WSUM, FLSUM, GSUM
      WRITE (IO, 6382)
      WSUM = 0.0
      FLSUM = 0.0
      GSUM = 0.0
      FSUM = 0.0
      YSUM = 0.0
      RSUM = 0.0
 3005 CONTINUE
      LAST = IDAY
      KAT = 1
 2500 CONTINUE
 3050 CONTINUE
      IY = IYEAR
C**
C     WRITE OUT ANNUAL SUMMARY:
C**
      IF (CONTOL .NE. 1) GO TO 3060
      WRITE (IO, 6340) IYEAR, RSUM
      GO TO 1606
 3060 CONTINUE
      IF (CONTOL .NE. 2) GO TO 3070
      WRITE (IO, 6355) IYEAR
 3070 CONTINUE
      WRITE (IO, 6370) IYEAR, FSUM, YSUM, RSUM
C**
C     PRINT OUT ACID STORAGE IN EACH BLOCK OF THE SYSTEM
C**
      DO 3201 I = 1, NFEET
      DO 3201 J = 1, NLAYER
      WRITE (IO, 6350) (STORE (I,J,K), K = 1, NDEPTH)
 3201 CONTINUE
      GO TO 1606
C**
C     WRITE OUT MESSAGE TO DENOTE END OF PROGRAM EVALUATION
C**
 2200 CONTINUE
      WRITE (IO, 6360)
C**
C     IF INITIAL ACID STORAGE IS NEEDED TO PREDICT ACID LOAD REMOVAL,
C        PUNCH OUT DATA CARDS, OTHERWISE STOP THE PROGRAM.
C**
      IF (CONTOL .LT. 3) GO TO 3217
      IF (NPUNCH .EQ. 0) GO TO 3217
      DO 3217 I = 1, NFEET
      DO 3217 J = 1, NLAYER
      WRITE (IP, 7000) (STORE (I,J,K), K = 1, NDEPTH)
 3217 CONTINUE
      STOP
 5100 FORMAT (I5)
 5110 FORMAT (8F10.5)
 5120 FORMAT (12F5.2)
 5210 FORMAT (F10.0, 2F10.5)
 5310 FORMAT (4I5)
 5320 FORMAT (2F5.2, F15.5, 3F10.5)
 5330 FORMAT (4F15.5)
 5340 FORMAT (2A4, 2X, 3F10.4)
 5130 FORMAT (1X, A4, 1X, I2, 2X, 4F10.5, I4)
 6300 FORMAT (1H1, ' THE FOLLOWING IS A DESCRIPTION OF THE MINE',/
     1' BEING MODELED.  THE LAYERS ARE COUNTED FROM THE BOTTOM.',//
     2' SECTION  LAYER  MATERIAL  ELEVATION  K(RATE)', 3X,'VOID',/
     328X, 'FEET')
6301 FORMAT (3X, I2, 7X, I2, 3X, 2A4, 3X, F5.2, 4X, F8.6, 2X, F7.3)
6305 FORMAT (10 (3X, F8.4))
6302 FORMAT (//F10.2///)
6100 FORMAT (3X, A4, I5, 3X, 2F10.4)
6110 FORMAT (//, 5X, 'INCHES OF WATER ENTERING STORAGE IS',F6.2//)
6200 FORMAT (3X, A4, I5, 3X, F10.2)
6350 FORMAT (3X, A4, I5, 3X, F6.0, 4(3X, F10.5))
6341 FORMAT (//, 5X, 'DRAINAGE FLOW DURING MONTH IS', F10.0, 'GALLONS',
     1/ 5X, 'ACID REMOVAL DURING MONTH IS', F10.0, 'POUNDS',/ 5X, 'WATER
     2 ENTERING STORAGE IS', F6.2, 'INCHES',//)
6345 FORMAT (5X, 'ACID REMOVED BY LEACHING IS', F10.0, 'POUNDS',/ 5X,
     1'ACID REMOVED BY FLOODING IS', F10.0, 'POUNDS',/ 5X, 'ACID REMOVED
     2 BY GRAVITY DIFFUSION IS', F10.0, 'POUNDS',///)
6340 FORMAT (////5X, 'SUMMARY OF DATA FOR', I4,//5X, 'WATER ENTERING ST
     1ORAGE IS', F6.2, 'INCHES'////)
6355 FORMAT (////5X, 'THIS IS THE END OF CALCULATION FOR TANK IN YEAR O
     1F ', I4,////)
6370 FORMAT (////5X, 'SUMMARY OF DATA FOR', I4,//5X, 'DRAINAGE FLOW DUR
     1ING YEAR IS', F10.0, 'GALLONS', //5X, 'ACID LOAD DURING YEAR IS',
     2F10.0, 'POUNDS',//5X, 'WATER ENTERING STORAGE IS', F6.2, 'INCHES',
     3////)
6360 FORMAT (1H1, '   TERMINATION CARD REACHED ')
6380 FORMAT (1H1,///5X, 'DATE',6X, 'RAIN, IN,', 4X, 'ADD, IN.',///)
6381 FORMAT (1H1, ///5X,'DATE', 6X, 'TANK, IN.',///)
6382 FORMAT (1H1,///5X, 'DATE', 6X, 'FLOW, GPD', 2X, 'ACID, LBS',4X,
     1'RAIN, IN.',///)
7000 FORMAT (8F10.2)
     END
```

Subroutine - DAYS

```
      SUBROUTINE DAYS
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, RTIME, TMEAN,AGO,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      IF( AGO .EQ. BLANK ) GO TO 2240
C  CHECK TO SEE IF MONTH HAS CHANGED
 2210 IF( AGO   - FEB) 2215, 2214, 2215
 2214 KEEP = 28
      GO TO 2230
 2215 IF(AGO .EQ. SEPT .OR. AGO .EQ. NOV .OR. AGO
     1 .EQ. APR .OR. AGO .EQ. JUNE) GO TO 2218
      KEEP = 31
      GO TO 2230
 2218 KEEP = 30
 2230 CONTINUE
      IF( AMONTH - AGO ) 2205, 2201, 2205
 2201 LTHETA = IDAY - LAST
      GO TO 2235
 2205 LTHETA =  KEEP - LAST + IDAY
 2235 CONTINUE
 2240 CONTINUE
      AG = AGO
      AGO =  AMONTH
      FLAG = 0.0
      AFLAG = 0.0
      IF(AGO .EQ. OCT ) AFLAG = 1.
      IF(AGO .EQ. NOV ) AFLAG = 1.
      IF(AGO .EQ. DEC ) AFLAG = 1.
      IF(AGO .EQ. JAN ) AFLAG = 1.
      IF(AGO .EQ. FEB ) AFLAG = 1.
      IF(AGO .EQ. MAR ) AFLAG = 3.
      IF(AGO .EQ. APR ) AFLAG = 2.
      RETURN
      END
```

Subroutine- EVAP

```
      SUBROUTINE EVAP (PEVAP)
C  SUBROUTINE ESTIMATES POTENTIAL EVAPOTRANSPIRATION
C  USING THORNTHWAITE METHOD
      REAL  BLANK, END, YEAR, JAN, FEB, MAR, APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CA/ BLANK,END,YEAR,JAN,FEB,MAR,APR,
     2 MAY, JUNE, JULY, AUG, SEPT, OCT, NOV, DEC
      COMMON/CB/ AMONTH, AG,RAIN, RTIME, TMEAN,AGC,
     1 TANKC, RSUM, RSUMA, FLAG, AFLAG, WSHED, PWHC,
     2 PWATER, LAST, KEEP, LTHETA, IDAY
      COMMON /CC/ VAP(12)
      IF( AMONTH - JAN ) 2, 1, 2
  1   PEVAP = VAP( 1)
      RETURN
  2   IF( AMONTH - FEB ) 4, 3, 4
  3   PEVAP = VAP( 2)
      RETURN
  4   IF( AMONTH - MAR ) 6, 5, 6
  5   PEVAP = VAP( 3)
      RETURN
  6   IF( AMONTH - APR ) 8, 7, 8
  7   PEVAP = VAP( 4)
      RETURN
  8   IF( AMONTH - MAY ) 10, 9, 10
  9   PEVAP = VAP( 5)
      RETURN
 10   IF( AMONTH - JUNE) 12, 11, 12
 11   PEVAP = VAP( 6)
      RETURN
 12   IF( AMONTH - JULY) 14, 13, 14
 13   PEVAP = VAP( 7)
      RETURN
 14   IF( AMONTH - AUG ) 16, 15, 16
 15   PEVAP = VAP( 8)
      RETURN
 16   IF( AMONTH - SEPT) 18, 17, 18
 17   PEVAP = VAP( 9)
      RETURN
 18   IF( AMONTH - OCT ) 20, 19, 20
 19   PEVAP = VAP(10)
      RETURN
 20   IF( AMONTH - NOV ) 22, 21, 22
 21   PEVAP = VAP(11)
      RETURN
 22   PEVAP = VAP(12)
      RETURN
      END
```

Subroutine REMOVE

```
      SUBROUTINE REMOV (DSLV, FLOW, M)
C**
C     THIS SUBROUTINE IS TO CALCULATE THE DAILY WATER BALANCE, ADD,
C        FLOW RATES, AND FRACTION OF PRODUCTS REMOVED EACH DAY BY
C        LEACHING.
C**
      REAL BLANK, END, YEAR, JAN, FEB, MAR, APR, MAY, JUNE, JULY, AUG,
     1SEPT, OCT, NOV, DEC
C**
      INTEGER CONTOL
C**
      COMMON/CA/ BLANK, END, YEAR, JAN, FEB, MAR, APR, MAY, JUNE, JULY,
     1AUG, SEPT, OCT, NOV, DEC
C**
      COMMON/CB/ ADD, AFLAG, AG, AGO, AMONTH, CONTOL, FLAG, IDAY, KEEP,
     1LAST, LTHETA, PWATER, PWHC, RAIN, RSUM, RSUMA, RTIME, TANK, TMEAN
     2, WSHED
C**
      EXTERNAL EVAP
C**
C     DEFINE INITIAL CONDITIONS AND REMOVE OLD VALUES FROM COMPUTER
C        STORAGE.
C     SNOW IS PRECEPITATION IN THE FORM OF SNOW
C     CON5 AND A ARE CALCULATIONAL CONSTANTS
C**
      SNOW = 0.0
      CON5 = WSHED * 7.5 / 12.0
      A = 4203. / 528.
      RETURN
      ENTRY REMOVE (DSLV, FLOW, M)
C**
C     CALCULATE DAILY POTENTIAL EVAPOTRANSPIRATION.

C     SUBROUTINE EVAP IS TO CALCULATE POTENTIAL EVAPORATION AND IT
C        RETURNS A MONTHLY AVERAGE POTENTIAL VALUE.
C**
      CALL EVAP (PEVAP)
C**
C     SUBTRACT EVAPORATION FROM ROOT STORAGE.
C     DEFICT IS DEFFICIENCY OF WATER IN ROOT STORAGE.
C**
      DEFICT = PWHC - PWATER
      IF (DEFICT .LT. 0.0) DEFICT = 0.0
C**
C     POTENTIAL EVAPOTRANSPIRATION DEPENDS ON MOISTURE CONTENT OF
C        GROUND.  THE EFFICIENCY FACTOR (EFF) IS FOUND TO BE EQUAL
C        TO PWATER / PWHC.  THE DAILY PEVAP IS EQUAL TO PEVAP / 30 *EFF.
```

```
C**
      EFF = PWATER / PWHC
      PEVAP = PEVAP / 30.
      PEVAP = PEVAP * EFF
C**
C     SOIL LAYER WATER BALANCE:
C     INPUT: RAIN OR SNOW
C     OUTPUT: RUNOFF, PEVAP, AND ADD
C     ADD IS WATER ENTERING STORAGE (TANK) AND IT IS A FUNCTION OF
C        TMEAN AND WOVERW.
C**
      RATE = RAIN / RTIME
      IF (RATE .GE. 0.25) RAIN = 0.25 * RTIME
C**
C     IF TMEAN IS BELOW FREEZING, ANY PRECEPITATION IS TREATED AS SNOW
C     SWMELT IS AMOUNT OF MELTED SNOW
C     RUNOFF IS WATER RUNOFF FROM OVER-BURDEN
C     EMRNF IS EXCESS WATER CONTENT MINUS RUNOFF

C     FADD IS TEMPERATURE FACTOR FOR WATER ENTERING STORAGE
C**
      IF (TMEAN .GT. 32.) GO TO 3092
      SNOW = RAIN + SNOW
      RAIN = 0.0
      SWMELT = 0.0
      RUNOFF = 0.0
      EMRNF = 0.0
      FADD = 0.075
      GO TO 3097
 3092 CONTINUE
C**
C     IF TMEAN IS ABOVE FREEZING, PROCEED WITH THE FOLLOWING:
C     IF RAINFALL IS GREATER THAN DEFICT, THE DIFFERENCE IS EXCS.  92
C        PERCENT OF THE EXCS IS ASSUMED TO BE RUNOFF AND THE REST
C        (EMRNF) IS ADDED TO THE BALANCE.
C**
      EXCS = RAIN - DEFICT
      IF (EXCS) 3093, 3093, 3094
 3093 EXCS = 0.0
 3094 RUNOFF = 0.92 * EXCS
      EMRNF = EXCS - RUNOFF
C**
C     CALCULATE FADD AS A FUNCTION OF TEMPERATURE.  FOR DESCRIPTION OF
C        THE DEVELOPMENT, SEE CHAPTER V OF THE TEXT.
C**
      IF (TMEAN .GE. 45.) FADD = 0.8
      IF (TMEAN .LT. 45. .AND. TMEAN .GT. 32.) FADD = 0.0557 * TMEAN
     1- 1.707
C**
C     IF SNOW FROM PREVIOUS DAYS MELTS DURING TMEAN ABOVE FREEZING MARK,
C        ONE TENTH OF AN INCH IS MELTED FOR EVERY DEGREE DAY.
```

```
C**
      IF (SNOW) 3095, 3095, 3096
 3095 SWMELT = 0.0
      GO TO 3097
 3096 SWMELT = 0.1 * (TMEAN - 32.)
      IF (SWMELT .GT. SNOW) SWMELT = SNOW
      SNOW = SNOW - SWMELT
C**
C     CALCULATE FADD AS A FUNCTION OF WOVERW = PWATER / PWHC.  SEE
C        CHAPTER V OF THE TEXT FOR REFERENCE.
C**
 3097 CONTINUE
      WOVERW = PWATER / PWHC
C**
C     COMBINE THE EFFECTS OF TMEAN AND WOVERW TO OBTAIN ADD:
C**
      ADD = FADD * (0.458 * WOVERW - 0.128)
      IF (ADD) 3090, 3090, 3091
 3090 ADD = 0.0
 3091 CONTINUE
C**
C     INCLUDE DAILY ADD IN MONTHLY AND ANNUAL ADD TOTAL.
C**
      RSUM = RSUM + ADD
      RSUMA = RSUMA + ADD
C**
C     FORMULATE THE SOIL LAYER WATER BALANCE BASED ON THE INPUTS AND
C        OUTPUTS DESCRIBED ABOVE.
C**
      PWATER = RAIN - RUNOFF - PEVAP - ADD + PWATER + EMRNF + SWMELT
      IF (PWATER .GT. 0.0) GO TO 3076
      PWATER = 0.0
 3076 CONTINUE
C**
C     IF ONLY ADD IS DESIRED (CONTOL = 1), PRINT OUT THE RESULTS BY
C        RETURNING TO THE MAIN PROGRAM.
C**
      IF (CONTOL .EQ. 1) GO TO 3077
C**
C     IF VALUES OF TANK ARE DESIRED TO BE USED TO EVALUATE TANK-HEAD
C        RELATIONSHIP, PROCEED WITH THE FOLLOWING:
C**
      IF (CONTOL .GT. 2) GO TO 3078
      TANK = TANK + ADD
      FLOW = CONFH * TANK
      TANK = TANK - FLOW
      GO TO 3077
 3078 CONTINUE
C**
C     IF FLOW AND DSLV ARE DESIRED, PROCEED WITH THE FOLLOWING:
```

```
C**
      TANK = TANK + ACC
      IF (TANK .LT. 0.55) HEAD = TANK
      IF (TANK .GE. 0.55) HEAD = 32.1 * TANK - 17.1
      FLOW = CONFH * HEAD
      TANK = TANK - FLOW
      DSLV = 0.0002 * (FLOW - HEADMI)
 3077 CONTINUE
      FLOW = FLOW * CON5
C**
C     RETURN TO THE MAIN PROGRAM WITH APPROPRIATE VALUES.
C**
      RETURN
      END
```

Sample Output - Auger Hole #1

```
Date              Flow          Acid Load       Rain
               (gal/day)        (lbs/day)       (in.)
JAN     1        103.           0.05580         0.0
JAN     2        107.           0.05687         0.0
JAN     3        109.           0.05825         0.0
JAN     4        128.           0.06128         0.0
JAN     5        169.           0.07015         0.0
JAN     6        194.           0.08614         0.0
JAN     7        185.           0.09516         0.0
JAN     8        175.           0.09931         0.0
JAN     9        166.           0.10016         0.0
JAN    10        157.           0.09892         0.0
JAN    11        148.           0.09638         0.0
JAN    12        148.           0.09436         0.0
JAN    13        150.           0.09400         0.24000
JAN    14        158.           0.09403         0.54000
JAN    15        150.           0.09371         0.0
JAN    16        148.           0.09222         0.0
JAN    17        146.           0.09097         0.0
JAN    18        145.           0.08989         0.0
JAN    19        143.           0.08896         0.0
JAN    20        141.           0.08815         0.0
JAN    21        139.           0.08666         0.0
JAN    22        137.           0.08543         0.0
JAN    23        136.           0.08440         0.0
JAN    24        128.           0.08268         0.0
JAN    25        121.           0.08064         0.0
JAN    26        127.           0.07972         0.0
JAN    27        120.           0.07831         0.0
JAN    28        114.           0.07698         0.0
JAN    29        110.           0.07545         0.0
JAN    30        113.           0.07443         0.12000
JAN    31        110.           0.07352         0.0

GALLONS OF FLOW DURING MONTH IS      4324.
POUNDS OF ACID DURING MONTH IS    2.6
INCHES OF RAIN ENTERING STORAGE IS  1.09


ACID REMOVED BY INUNDATION    0.652
ACID REMOVED BY GRAVITY DIFFUSION    1.175
ACID REMOVED BY LEACHING    1.550
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
FEB	1	149.	0.07820	0.0
FEB	2	232.	0.10697	0.60000
FEB	3	209.	0.12262	0.0
FEB	4	189.	0.12598	0.0
FEB	5	173.	0.12495	0.0
FEB	6	177.	0.12435	0.0
FEB	7	182.	0.12675	0.02000
FEB	8	248.	0.15362	0.27000
FEB	9	320.	0.21009	0.54000
FEB	10	300.	0.23747	0.04000
FEB	11	265.	0.23679	0.0
FEB	12	236.	0.23849	0.0
FEB	13	212.	0.22575	0.0
FEB	14	191.	0.20714	0.0
FEB	15	328.	0.26024	0.28000
FEB	16	298.	0.26705	0.0
FEB	17	255.	0.26188	0.0
FEB	18	344.	0.30580	0.0
FEB	19	409.	0.37199	0.0
FEB	20	352.	0.39157	0.0
FEB	21	305.	0.39188	0.0
FEB	22	306.	0.37315	0.0
FEB	23	305.	0.36510	0.0
FEB	24	302.	0.35193	0.0
FEB	25	298.	0.34030	0.0
FEB	26	259.	0.31627	0.0
FEB	27	226.	0.29908	0.0
FEB	28	199.	0.25840	0.0

GALLONS OF FLOW DURING MONTH IS 7262.
POUNDS OF ACID DURING MONTH IS 6.9
INCHES OF RAIN ENTERING STORAGE IS 1.91

ACID REMOVED BY INUNDATION 5.477
ACID REMOVED BY GRAVITY DIFFUSION 0.549
ACID REMOVED BY LEACHING 2.774

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
MAR	1	273.	0.24839	0.0
MAR	2	325.	0.28166	0.11000
MAR	3	361.	0.31773	0.0
MAR	4	393.	0.35438	0.61000
MAR	5	401.	0.39576	0.17000
MAR	6	378.	0.41299	0.0
MAR	7	358.	0.41703	0.0
MAR	8	340.	0.41317	0.0
MAR	9	323.	0.40482	0.0
MAR	10	307.	0.38048	0.0
MAR	11	292.	0.34945	0.0
MAR	12	286.	0.32074	0.54000
MAR	13	249.	0.29445	0.0
MAR	14	219.	0.26389	0.0
MAR	15	193.	0.23377	0.0
MAR	16	172.	0.20719	0.0
MAR	17	153.	0.18327	0.0
MAR	18	197.	0.17147	0.25000
MAR	19	297.	0.18779	0.0
MAR	20	366.	0.23542	0.0
MAR	21	412.	0.29991	0.0
MAR	22	439.	0.37275	0.0
MAR	23	426.	0.42403	0.06000
MAR	24	393.	0.43078	0.0
MAR	25	364.	0.42350	0.11000
MAR	26	385.	0.42513	0.0
MAR	27	355.	0.41155	0.0
MAR	28	328.	0.39511	0.75000
MAR	29	330.	0.38124	0.31000
MAR	30	299.	0.34913	0.0
MAR	31	372.	0.35357	0.0

GALLONS OF FLOW DURING MONTH IS 9975.
POUNDS OF ACID DURING MONTH IS 10.3
INCHES OF RAIN ENTERING STORAGE IS 2.68

ACID REMOVED BY INUNDATION 8.175
ACID REMOVED BY GRAVITY DIFFUSION 0.213
ACID REMOVED BY LEACHING 3.992

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
APR	1	420.	0.39743	0.15000
APR	2	434.	0.43801	1.76000
APR	3	450.	0.47699	0.0
APR	4	458.	0.50781	0.0
APR	5	458.	0.53044	0.0
APR	6	452.	0.54526	0.16000
APR	7	517.	0.48593	0.05000
APR	8	557.	0.44264	0.0
APR	9	576.	0.41175	0.0
APR	10	577.	0.38707	0.0
APR	11	567.	0.36602	0.0
APR	12	547.	0.34605	0.0
APR	13	521.	0.32665	0.14000
APR	14	500.	0.30760	0.06000
APR	15	478.	0.37526	0.0
APR	16	451.	0.41475	0.0
APR	17	422.	0.43157	0.0
APR	18	392.	0.41769	0.0
APR	19	361.	0.39546	0.30000
APR	20	349.	0.37320	0.54000
APR	21	367.	0.35947	0.0
APR	22	372.	0.34806	0.0
APR	23	368.	0.33793	0.37000
APR	24	380.	0.33500	0.54000
APR	25	415.	0.34890	0.0
APR	26	432.	0.37725	0.0
APR	27	435.	0.39951	0.0
APR	28	429.	0.41457	0.25000
APR	29	430.	0.42545	0.0
APR	30	420.	0.42750	0.0

```
GALLONS OF FLOW DURING MONTH IS     13535.
POUNDS OF ACID DURING MONTH IS  12.2
INCHES OF RAIN ENTERING STORAGE IS  3.42


ACID REMOVED BY INUNDATION    9.351
ACID REMOVED BY GRAVITY DIFFUSION   0.0
ACID REMOVED BY LEACHING   5.346
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
MAY	1	402.	0.41281	0.0
MAY	2	378.	0.38864	0.16000
MAY	3	361.	0.36277	0.0
MAY	4	338.	0.33610	0.0
MAY	5	313.	0.30870	0.0
MAY	6	285.	0.27483	0.0
MAY	7	257.	0.24715	0.0
MAY	8	229.	0.22132	0.0
MAY	9	202.	0.19665	0.0
MAY	10	176.	0.17413	0.0
MAY	11	151.	0.15404	0.0
MAY	12	127.	0.13621	0.30000
MAY	13	124.	0.12187	0.37000
MAY	14	141.	0.11175	0.05000
MAY	15	151.	0.10458	0.0
MAY	16	153.	0.09906	0.48000
MAY	17	179.	0.09718	0.0
MAY	18	192.	0.09722	0.04000
MAY	19	198.	0.09858	0.0
MAY	20	196.	0.09959	0.0
MAY	21	189.	0.09912	0.0
MAY	22	177.	0.09746	0.0
MAY	23	162.	0.09489	0.0
MAY	24	146.	0.09140	0.65000
MAY	25	170.	0.09120	0.0
MAY	26	182.	0.09254	0.03000
MAY	27	187.	0.09397	0.0
MAY	28	184.	0.09500	0.0
MAY	29	176.	0.09475	1.48000
MAY	30	188.	0.09606	0.0
MAY	31	193.	0.09753	0.0

```
GALLONS OF FLOW DURING MONTH IS      6507.
POUNDS OF ACID DURING MONTH IS    5.1
INCHES OF RAIN ENTERING STORAGE IS  1.34


ACID REMOVED BY INUNDATION    1.149
ACID REMOVED BY GRAVITY DIFFUSION    0.669
ACID REMOVED BY LEACHING    3.029
```

Date	Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
JUNE 1	193.	0.09986	0.0
JUNE 2	190.	0.10052	0.12000
JUNE 3	187.	0.10088	0.45000
JUNE 4	191.	0.10154	0.10000
JUNE 5	193.	0.10229	0.0
JUNE 6	191.	0.10282	0.0
JUNE 7	185.	0.10293	0.0
JUNE 8	178.	0.10205	0.0
JUNE 9	168.	0.10046	0.0
JUNE 10	158.	0.09832	0.0
JUNE 11	146.	0.09576	0.0
JUNE 12	135.	0.09291	0.0
JUNE 13	123.	0.08981	0.25000
JUNE 14	117.	0.08696	0.15000
JUNE 15	113.	0.08448	0.80000
JUNE 16	126.	0.08363	0.0
JUNE 17	134.	0.08367	0.0
JUNE 18	137.	0.08399	0.0
JUNE 19	136.	0.08429	0.0
JUNE 20	132.	0.08433	0.0
JUNE 21	126.	0.08397	0.0
JUNE 22	119.	0.08320	0.0
JUNE 23	111.	0.08204	0.0
JUNE 24	102.	0.08052	0.0
JUNE 25	93.	0.07868	0.0
JUNE 26	83.	0.07656	0.27000
JUNE 27	80.	0.07471	0.78000
JUNE 28	94.	0.07439	0.0
JUNE 29	102.	0.07489	0.0
JUNE 30	106.	0.07566	0.0

```
GALLONS OF FLOW DURING MONTH IS      4148.
POUNDS OF ACID DURING MONTH IS   2.7
INCHES OF RAIN ENTERING STORAGE IS  0.92

ACID REMOVED BY INUNDATION    0.092
ACID REMOVED BY GRAVITY DIFFUSION    1.023
ACID REMOVED BY LEACHING    2.152
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
JULY	1	106.	0.07638	0.0
JULY	2	104.	0.07685	0.23000
JULY	3	105.	0.07738	0.12000
JULY	4	105.	0.07794	0.75000
JULY	5	121.	0.07985	0.0
JULY	6	130.	0.08229	0.0
JULY	7	134.	0.08481	0.0
JULY	8	133.	0.08688	0.0
JULY	9	130.	0.08818	0.0
JULY	10	124.	0.08885	0.0
JULY	11	117.	0.08877	0.06000
JULY	12	110.	0.08816	0.0
JULY	13	102.	0.08704	0.0
JULY	14	93.	0.08547	0.0
JULY	15	84.	0.08352	0.30000
JULY	16	81.	0.08184	0.64000
JULY	17	92.	0.08151	0.0
JULY	18	98.	0.08183	0.0
JULY	19	100.	0.08231	0.0
JULY	20	99.	0.08267	0.31000
JULY	21	102.	0.08340	0.0
JULY	22	102.	0.08407	0.0
JULY	23	100.	0.08442	0.0
JULY	24	95.	0.08440	0.32000
JULY	25	97.	0.08458	0.0
JULY	26	95.	0.08468	0.0
JULY	27	91.	0.08450	0.50000
JULY	28	98.	0.08502	0.0
JULY	29	100.	0.08571	0.10000
JULY	30	102.	0.08655	0.50000
JULY	31	112.	0.08833	0.0

```
GALLONS OF FLOW DURING MONTH IS     3263.
POUNDS OF ACID DURING MONTH IS   2.6
INCHES OF RAIN ENTERING STORAGE IS  0.82

ACID REMOVED BY INUNDATION   0.022
ACID REMOVED BY GRAVITY DIFFUSION    1.299
ACID REMOVED BY LEACHING   1.868
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
AUG	1	117.	0.09046	0.0
AUG	2	118.	0.09235	0.0
AUG	3	117.	0.09377	0.21000
AUG	4	117.	0.09505	0.0
AUG	5	115.	0.09596	0.0
AUG	6	111.	0.09621	0.0
AUG	7	105.	0.09583	0.0
AUG	8	98.	0.09490	0.0
AUG	9	90.	0.09348	1.50000
AUG	10	117.	0.09530	1.00000
AUG	11	158.	0.10260	0.0
AUG	12	187.	0.11478	0.0
AUG	13	205.	0.12867	0.0
AUG	14	215.	0.14404	0.0
AUG	15	218.	0.15649	0.0
AUG	16	217.	0.16616	0.0
AUG	17	211.	0.17319	0.0
AUG	18	203.	0.17483	0.03000
AUG	19	194.	0.17516	0.0
AUG	20	183.	0.17220	0.0
AUG	21	171.	0.16734	0.12000
AUG	22	161.	0.16159	0.88000
AUG	23	171.	0.15895	0.0
AUG	24	175.	0.15724	0.0
AUG	25	175.	0.15586	0.0
AUG	26	171.	0.15441	0.0
AUG	27	165.	0.15177	0.0
AUG	28	156.	0.14824	0.0
AUG	29	147.	0.14405	0.0
AUG	30	136.	0.13936	0.0
AUG	31	125.	0.13435	0.0

```
GALLONS OF FLOW DURING MONTH IS      4848.
POUNDS OF ACID DURING MONTH IS   4.1
INCHES OF RAIN ENTERING STORAGE IS  1.22


ACID REMOVED BY INUNDATION    0.605
ACID REMOVED BY GRAVITY DIFFUSION    1.490
ACID REMOVED BY LEACHING    3.018
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
SEPT	1	114.	0.12900	0.0
SEPT	2	103.	0.12367	0.0
SEPT	3	93.	0.11841	0.05000
SEPT	4	84.	0.11341	0.50000
SEPT	5	87.	0.10982	0.05000
SEPT	6	89.	0.10722	0.0
SEPT	7	89.	0.10518	0.0
SEPT	8	87.	0.10342	0.0
SEPT	9	83.	0.10174	0.0
SEPT	10	79.	0.10003	0.0
SEPT	11	78.	0.09865	0.0
SEPT	12	77.	0.09753	0.0
SEPT	13	76.	0.09660	0.0
SEPT	14	75.	0.09580	0.06000
SEPT	15	74.	0.09511	0.0
SEPT	16	73.	0.09450	0.0
SEPT	17	71.	0.09394	0.0
SEPT	18	70.	0.09340	0.19000
SEPT	19	69.	0.09294	0.10000
SEPT	20	68.	0.09256	0.17000
SEPT	21	68.	0.09229	0.0
SEPT	22	67.	0.09208	0.0
SEPT	23	66.	0.09190	0.0
SEPT	24	66.	0.09174	0.0
SEPT	25	64.	0.09156	0.0
SEPT	26	63.	0.09136	0.0
SEPT	27	62.	0.09114	1.29000
SEPT	28	65.	0.09133	0.0
SEPT	29	66.	0.09168	0.0
SEPT	30	67.	0.09212	0.0

```
GALLONS OF FLOW DURING MONTH IS     2294.
POUNDS OF ACID DURING MONTH IS   3.0
INCHES OF RAIN ENTERING STORAGE IS  0.40


ACID REMOVED BY INUNDATION   0.002
ACID REMOVED BY GRAVITY DIFFUSION   1.654
ACID REMOVED BY LEACHING   1.535
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
OCT	1	68.	0.09262	0.0
OCT	2	69.	0.09316	0.0
OCT	3	69.	0.09370	0.30000
OCT	4	70.	0.09431	0.0
OCT	5	71.	0.09496	0.0
OCT	6	72.	0.09565	0.0
OCT	7	72.	0.09632	0.0
OCT	8	73.	0.09697	0.0
OCT	9	73.	0.09758	0.0
OCT	10	73.	0.09819	0.55000
OCT	11	74.	0.09888	0.45000
OCT	12	76.	0.09978	0.0
OCT	13	78.	0.10084	0.0
OCT	14	83.	0.10238	0.81000
OCT	15	105.	0.10676	0.10000
OCT	16	123.	0.11346	0.0
OCT	17	136.	0.12096	0.0
OCT	18	145.	0.12884	0.0
OCT	19	151.	0.13686	0.0
OCT	20	154.	0.14368	0.11000
OCT	21	158.	0.14948	0.56000
OCT	22	168.	0.15663	0.02000
OCT	23	174.	0.16487	0.0
OCT	24	178.	0.17189	0.0
OCT	25	180.	0.17763	0.0
OCT	26	180.	0.18214	0.0
OCT	27	178.	0.18549	0.0
OCT	28	175.	0.18775	0.0
OCT	29	171.	0.18907	0.60000
OCT	30	176.	0.19070	0.73000
OCT	31	190.	0.19627	0.0

```
GALLONS OF FLOW DURING MONTH IS      3762.
POUNDS OF ACID DURING MONTH IS    4.1
INCHES OF RAIN ENTERING STORAGE IS  1.18


ACID REMOVED BY INUNDATION    0.480
ACID REMOVED BY GRAVITY DIFFUSION    1.893
ACID REMOVED BY LEACHING    2.725
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
NOV	1	200.	0.20550	0.0
NOV	2	206.	0.21355	0.60000
NOV	3	216.	0.22646	0.10000
NOV	4	219.	0.23685	0.03000
NOV	5	225.	0.25311	0.03000
NOV	6	229.	0.26637	0.03000
NOV	7	231.	0.27683	0.03000
NOV	8	233.	0.28492	0.03000
NOV	9	233.	0.29099	0.03000
NOV	10	232.	0.29538	0.09000
NOV	11	232.	0.29845	0.04000
NOV	12	231.	0.30042	0.0
NOV	13	229.	0.30138	0.04000
NOV	14	227.	0.30153	0.48000
NOV	15	219.	0.29401	0.32000
NOV	16	198.	0.28102	0.0
NOV	17	191.	0.26377	0.0
NOV	18	185.	0.25236	0.0
NOV	19	195.	0.24731	0.0
NOV	20	203.	0.24413	0.40000
NOV	21	198.	0.24079	0.0
NOV	22	198.	0.23428	0.04000
NOV	23	174.	0.22554	0.0
NOV	24	160.	0.21592	0.0
NOV	25	148.	0.20563	0.0
NOV	26	146.	0.19717	0.0
NOV	27	161.	0.19350	0.0
NOV	28	172.	0.19297	0.0
NOV	29	180.	0.19356	0.25000
NOV	30	190.	0.19712	0.0

```
GALLONS OF FLOW DURING MONTH IS      6039.
POUNDS OF ACID DURING MONTH IS   7.4
INCHES OF RAIN ENTERING STORAGE IS  1.50


ACID REMOVED BY INUNDATION    2.015
ACID REMOVED BY GRAVITY DIFFUSION    1.871
ACID REMOVED BY LEACHING    4.550
```

Date		Flow (gal/day)	Acid Load (lbs/day)	Rain (in.)
DEC	1	313.	0.29693	0.0
DEC	2	401.	0.45491	0.0
DEC	3	461.	0.64256	0.10000
DEC	4	505.	0.61660	0.20000
DEC	5	430.	0.74705	0.0
DEC	6	368.	0.76763	0.0
DEC	7	316.	0.74345	0.0
DEC	8	299.	0.69445	0.0
DEC	9	366.	0.71970	0.0
DEC	10	373.	0.73876	0.0
DEC	11	410.	0.79631	0.0
DEC	12	431.	0.87441	1.00000
DEC	13	432.	0.93447	0.0
DEC	14	449.	0.99303	0.0
DEC	15	384.	0.95938	0.0
DEC	16	358.	0.91320	0.26000
DEC	17	390.	0.89517	0.24000
DEC	18	389.	0.87829	0.0
DEC	19	466.	0.94354	0.0
DEC	20	453.	0.98499	0.0
DEC	21	387.	0.94276	0.0
DEC	22	444.	0.96832	0.88000
DEC	23	688.	0.91687	1.04000
DEC	24	638.	0.86089	0.0
DEC	25	545.	0.79382	0.0
DEC	26	468.	0.86658	0.0
DEC	27	404.	0.85846	0.0
DEC	28	351.	0.80769	0.0
DEC	29	307.	0.73306	0.0
DEC	30	270.	0.64038	0.0
DEC	31	239.	0.56915	0.0

GALLONS OF FLOW DURING MONTH IS 12734.
POUNDS OF ACID DURING MONTH IS 24.6
INCHES OF RAIN ENTERING STORAGE IS 3.22

ACID REMOVED BY INUNDATION 19.437
ACID REMOVED BY GRAVITY DIFFUSION 0.044
ACID REMOVED BY LEACHING 8.665

SUMMARY OF DATA FOR 1970

GALLONS OF FLOW DURING YEAR IS 78690.

POUNDS OF ACID DURING YEAR IS 85.

INCHES OF RAIN ENTERING STORAGE IS 19.69

APPENDIX D

INSTRUCTIONS FOR USE OF MAIN PROGRAM

The use of this program for predicting flow rates and acid loads at other sites is described in this appendix. The discussion presumes that the reader is familiar with the technical content of the model and needs only "nuts and bolts" information to use the computer program for his system.

The application of this program requires that the user furnish three kinds of information; i.e.,

1. specific program statements as described below,
2. data describing system, and
3. meteorological data.

The user must furnish statements identifying the input and output channels of his computer installation. These statements have the form

IN = Input channel number,

IO = Printed output channel number, and

IP = Punched output channel number.

The statements replace the IN, IO, and IP identities at the beginning of the program. These are channels 5, 6, and 7, respectively, in the Ohio State University computer system.

Since only portions of the total program are used in the process of developing the model, an integer control is used to select that portion of the program that is wanted. If only ADD is to be calculated, as is the case when Watershed is being evaluated, control (CONTOL) is 1. To calculate ADD and TANK, control = 2. For ADD, FLOW, and Acid Load, control = 3.

Description of the Input data cards are listed in Table 13.

TABLE 13

INPUT DATA FOR COMPUTER PROGRAM

I. To Generate ADD

	Variable	Format
Control Card, Columns 1 - 5	CONTOL	I 5
	Variable	Format
Card 1		
Columns 1 - 10	PWHC	F10.5
11 - 20	PWATER	F10.5
Card 2		
Columns 1 - 5, 6 - 10, etc.	VAP	F 5.2
Card 3 to end of weather data*		
Columns 2 - 5	AMONTH	A 4
7 - 8	IDAY	I 2
10 - 20	RAIN	F10.5
21 - 30	RTIME	F10.5
31 - 40	TMEAN	F10.5
41 - 50	OXY	F10.5
Final Card		
Columns 2 - 4	"END"	A 3

II. To Generate TANK

Card 1 to Card 2 are the same as in I, Control Card integer = 2

Card 3		
Columns 1 - 10	WSHED	F10.0
11 - 20	TANK	F10.5
21 - 30	CONFH	F10.5

Card 4 is the same as Card 3 in I.

Final Card is the same as Final Card in I.

III. To Calculate FLOW and Acid Load

Card 1 to Card 3 are the same as in II, Control Card integer = 3

Card 4		
Column 1 - 5	NFEET	I 5

TABLE 13 - (Continued)

	Variable	Format
Columns 6 - 10	NLAYER	I 5
11 - 15	NDEPTH	I 5
16 - 20	NPUNCH	I 5
Card 5		
Columns 1 - 5	DK	F 5.2
6 - 10	ALKALI	F 5.2
11 - 25	FLOWMI	F15.5
26 - 35	HEADMI	F10.5
36 - 45	PER	F10.5
46 - 55	WSLOPE	F10.5
Card 6		
Columns 1 - 15	DI	F15.5
16 - 30	TOP	F15.5
Card 7 to NLAYER + 7		
Columns 1 - 8	ROCK TYPE	2 A 4
11 - 20	ALT	F10.4
21 - 30	REACT	F10.4
31 - 40	PYCON	F10.5

Repeat Card 6 and Card 7 to Card NLAYER + 7 for NFEET - 1 times.

The Cards following Card NLAYER + 7 are the same as Card 3 in I.

Final Card is the same as Final Card in I.

* Summary card can be placed between the daily weather cards as frequently as desired. Their Format are:

Columns 2 - 5	"YEAR"	A 4
51 - 54	The year number	I 4

A set of NLAYER cards, one for each stratum or substratum, follows the initial data. In addition to the natural division between coal and shale layers, it is desirable to subdivide thick binder layers into thinner layers for computational purposes. In our test case, the coal layers were divided into sections of no greater than six-inch thickness. The natural shale layers were one to four inches thick so no division was necessary. Each card contains a brief alphameric description of the stratum, the elevation of the bottom of the stratum relative to a datum plane, the oxygen consumption in the material $\mu g\ O_2 \cdot hr^{-1} \cdot cm^{-3}$, and the void fraction of the binder.

The final batch of descriptive input data is the initial quantity of oxidation products stored in each incremental volume. If initial values are not known, they may be estimated by assuming they are zero (by inserting an appropriate number of blank data cards) and allowing the program to run for a simulated period of three to five years. Storage values will be built up in the STORE (I,J,K) array in this simulation. These values may be obtained as punched output by reading a positive value of NPUNCH on the first data card. The punched data may then be recycled as initial conditions.

Once the system has been described, day-to-day weather data are read into the program. Each daily data card contains the month and day, (AMONTH and IDAY), the inches of precipitation (RAIN), the hours of duration of the precipitation (RTIME), the mean temperature (TMEAN), and the oxygen mole fraction (OXY). Each of these data, except OXY, must be included on every card. OXY need only appear on the first card, and thereafter only when its value changes. The remaining data need only be read for positive changes (i.e., precipitation or temperature changes), otherwise, the program will assume zero rainfall and constant temperature. During warmer weather, it is adequate to assume the monthly average temperature since the chief program use of the temperature data is the calculation of freeze-thaw information.

The month must be read in as standard three- or four-letter notation: Jan, Feb, Mar, Apr, May, June, July, Aug, Sept, Oct, Nov, Dec. No periods are to be used in these abbreviations.

In addition to the weather cards, output control cards may be included in the data deck. On these cards the word "Year" is punched instead of the month, and the year number of the preceding year may be punched. Placing a "Year" card at the end of a block of data will give a printout of the summary for total flow and acid load since the previous "Year" card. Monthly reviews are always printed, so the "Year" card permits quarterly or annual totals to be printed. The final data card must contain the word "End" in the month slot to terminate calculations.

The first output from the program is an echo of the descriptive data. The normal output from the program is the daily flow rate, acid load, and the quantity of precipitation. In addition, monthly totals of flow and acid load are printed. The monthly acid load is also divided into the amount removed by each of the three removal mechanisms. The total reflects the alkalinity of the ground water so it is less than the sum of the three subtotals. As was mentioned above, provision has been made for printing longer-term summaries of flow and acid load data if such are desired.

APPENDIX E

EVALUATION OF PARAMETERS AND CONSTANTS FOR SUBROUTINE "REMOVE"

Based on the general principles stated in Section VI, daily drainage flow and acid load from an underground mine can be calculated with the help of a digital computer. Calculation of some of the important parameters and constants are illustrated below. Others are either self-explanatory or were outlined when describing the program itself.

PWHC: Provisional water holding capacity, or simply, the ability of the root structure in the soil alyer to hold water. A value of 10 inches for PWHC was used in the Morth model.[25] For the McDaniel's model of this report, a value of 4 inches was selected after a number of values were tried. PWHC's larger than 4 inches gave low levels of saturation for the winter months. On the other hand, PWHC values smaller than 4 inches gave excessive runoff. As a result, a PWHC of 4 inches was chosen for the model of the McDaniels complex.

PWATER: Moisture content in the soil layer in inches. This value varies with the soil layer water balance according to Eq. (16). During the winter months, the soil layer at the test site is usually close to saturation (with water) and PWATER should have a value close to PWHC. On the other hand, in the summer months PWATER will have its lowest value. In this model, soil layer water balance was started during the highly saturated period. PWHC values equal to 4 inches were used as the initial values.

PEVAP: Potential evaporation. Monthly PEVAP was estimated by the method of Thornthwaite and Mather.[42] SUBROUTINE EVAP chooses the appropriate value for a given month, which is divided by 30 to become the daily value. PEVAP is also proportional to the efficiency factor (EFF), which is the ratio of PWATER to PWHC.

FADD: Temperature factor for determining ADD. When temperatures are above 45°F, predominantly during June to October, a constant value for FADD of 0.8 is assumed. For temperatures below the freezing mark, occurring mostly in the months of November to March, water in the soil layer is frozen and less mobility results. A small fraction (FADD = 0.075) of the water content was assumed to go to storage. When temperatures are between 32 and 45°F, a linear relationship given by Eq. (26), was assumed between the mean temperature (TMEAN) and FADD.

$$\text{FADD} = 0.0557 * \text{TMEAN} - 1.707 \quad (32\text{-}45^\circ\text{F}). \qquad (26)$$

WOVERW: ratio of PWATER to PWHC. The amount of water leaving the soil layer as ADD was assumed to be a linear function of WOVERW as expressed by the equation

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$$\text{ADD} = \text{FADD} * (0.458 * \text{WOVERW} - 0.128) \qquad (27\text{A})$$

$$\text{ADD} = \text{FADD} * (1.38 * \text{WOVERW} - 0.38), \qquad (27\text{B})$$

where Eq. (27A) applies to the mine and auger holes in the McDaniels complex, and Eq. (27B) was used for the Decker No. 3. Constants for the ADD equation selected to either increase or decrease RUNOFF during the "wet" periods of the hydrologic year. The greater the amount of water removed from the soil layer per day, the more water that can be taken into the soil layer before it becomes saturated. In the case of mines with large watersheds or those with relatively level terrain above the mine, more of the precipitation will enter the soil layer and Eq. (27B) should be tried first.

WSHED: Watershed area in square feet through which water passes through the soil to provide drainage flow water. This is determined by the observed annual flow (or monthly flow during steady flow period) and the calculated water entering the aquifer over the same period. Since FLOW is in gallons and ADD is in inches, a conversion factor of 12/7.5 is used to give WSHED in square feet units. Before a predicted value for FLOW can be calculated, WSHED must be known. Therefore, the first step in applying the model must be the calculation of the annual ADD total. The values of WSHED used for the McDaniels Test Mine, auger holes, and Decker #3 Mine are listed in Table 14. Sample calculations using annual flow data and data points during a steady flow period are illustrated below using data from Auger Hole #1.

A. WSHED by annual flow data:

Annual ADD for 1970 = 19.69 inches
Observed 1970 total flow from Auger Hole #1 = 75.690 gallons

$$\text{WSHED} = \frac{75.690 \text{ gallons}}{19.69 \text{ inches}} \text{ x } \frac{\text{ft}^3}{7.5 \text{ gallons}} \text{ x } \frac{12 \text{ in.}}{\text{ft.}} = 6180 \text{ ft}^2$$

B. WSHED by data during steady flow period:

Monthly ADD for July, 1970 = 0.82 inch
Observed total outflow in July, 1970 from Auger Hole #1 = 3069 gallons

$$\text{WSHED} = \frac{3069 \text{ gallons}}{0.82 \text{ inch}} \text{ x } \frac{\text{ft}^2}{7.5 \text{ gallons}} \text{ x } \frac{12 \text{ in.}}{\text{ft.}} = 6000 \text{ ft}^2$$

TANK: Aquifer storage for drainage flow. The concept of TANK is hypothetical; therefore, a value representing aquifer storage, which is the source of drainage flow, cannot be determined by field measurements. The base value of TANK is not the most critical factor in the

TABLE 14

LIST OF CONSTANTS AND PARAMETERS

	McDaniels Test Mine	Auger Hole #1	Auger Hole #3	Auger Hole #4	Auger Hole #5	Auger Hole #6	Decker #3 Mine
WSHED (ft^2)	7,920	6,180	4,710	3,640	1,010	6,800	2,750,000
Base TANK (in.)	2.13	1.10	1.18	1.07	0.51	0.86	0.50
CONFH	0.0200	0.0236	0.0207	0.0240	0.1120	0.0392	0.0300
HEADMI (in.)	1.510 (150 gal)	0.931 (85 gal)	0.491 (30 gal)	0.550 (30 gal)	0. (0 gal)	0.420 (70 gal)	0.660 (34,000 gal)
WSLOPE	0.15	0.08	0.12	0.07	0.10	0.16	0.10
PER	1.8	1.5	1.6	1.4	1.7	2.0	2.5
FLOWMI (gal)	300	115	60	80	0	95	290,000

relation for predicting FLOW, but the relationship of TANK - HEAD is most important. Certainly, the better the base value for TANK, the better the TANK - HEAD relationship can be described. The procedures for estimating TANK from experimental data are outlined in the following steps:

1. During a steady flow period, values of TANK are comparatively constant. In light of this, the generation of the base value of TANK is best started in this period.

2. The program (i.e., SUBROUTINE REMOVE) was run for a period of four years. Auger Hole #1 will be used to illustrate how the values for constants used in FLOW calculations were obtained.

    a. assume TANK = 0.82

    This is a hypothetical value, not the base value discussed in the above paragraphs. The actual value is not critical, but some value must be assumed. For reference purposes, 0.82, which was the total monthly ADD in July, 1970, was chosen to be the value of TANK.

    b. Temperature and rainfall data used for the period were a repetition of 1970 data.

    c. The relation: FLOW = CONFH * TANK was used. The value of CONFH was determined by

    $$\frac{\text{FLOW}}{\text{TANK}} = \frac{0.026}{0.82} = 0.033,$$

    where 0.026 is the July, 1970, average daily flow in inches obtained from

    $$\frac{3960 \text{ gallons}}{\text{month}} \times \frac{\text{month}}{30 \text{ days}} \times \frac{\text{ft}^3}{7.5 \text{ gallons}} \times \frac{1}{6180 \text{ ft}^2} \times \frac{12 \text{ in.}}{\text{ft.}}$$

    $= 0.026$ inches.

    d. After the first two years of program running period, values of TANK in July, 1969, and 1970, became "steady" values, ranging between 1.15 and 1.06. An average value equal to 1.1 was used as the assumed base value of TANK during the steady flow period.

3. CONFH: Constant relating flow and aquifer storage. During steady flow period, TANK (1.1) and the average

daily flow (0.026) are known. Then, CONFH is the quotient of 0.026/1.1 = 0.0236 for Auger Hole #1. Other CONFH values are listed in Table 14.

HEAD: Head of water stored in the aquifer. Auger Hole #1 is used for the purpose of illustration. The procedures to establish the relationship between TANK and HEAD are listed as follows:

1. Up to this point, values for WSHED (6180 ft^2), base TANK (1.1 inches), and CONFH (0.0236) are known. With these parameters and constants, FLOW in gallons per day and daily TANK in inches can be obtained from the output of the program.

2. Outputs for the steady flow period were examined. The examination was conducted in the following manner.

   a. Convert the observed flow data from gallons per day to inches of water per day by the relation

   $$\text{WSHED} * \frac{7.5}{12} * \text{CONFH};$$

   for example, the observed FLOW was 350 gallons per day on March 8, 1970. The corresponding HEAD to give this FLOW will be

$$\frac{350 \text{ gallons}}{\text{day}} \times \frac{1}{6180 \text{ ft}^2} \times \frac{12 \text{ in.}}{\text{ft.}} \times \frac{\text{ft}^3}{7.5 \text{ gal.}} \times \frac{1}{0.0236} \times 1 \text{ day}$$

$$= 3.84 \text{ inches.}$$

   b. From the output of the program, the value of TANK was found to be 1.2 inches on March 8,1970.

   c. The values from steps a and b above were located on HEAD vs. TANK plot as one point to establish the relationship between HEAD and TANK.

   d. Several other points were obtained by repeating steps a through c; then a diagram (as shown in Fig. 30) was constructed.

3. Based on the data shown in Fig. 30, two intersecting straight lines were used to represent the curve for the sake of ease in formulating the equations which were used in the computer program.

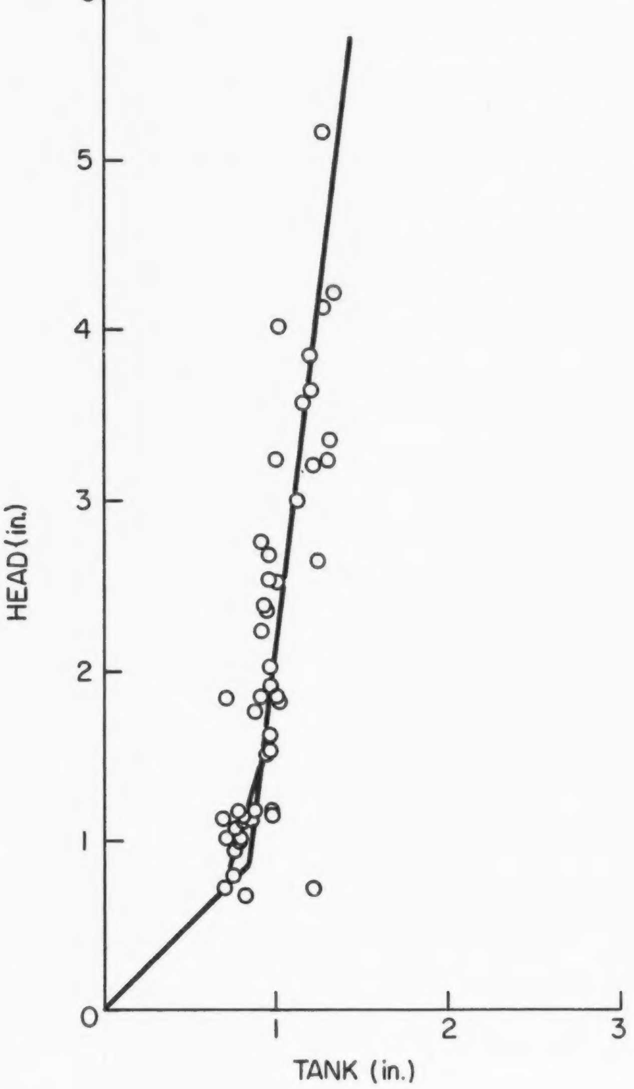

Figure 30 - HEAD vs TANK from Experimental Data

DSLV: Fraction of products removed each day by leaching. At and below the minimum flow rate, the amount of acid removed by leaching was assumed to be negligible. Above this minimum flow (HEADMI), leaching is an important contribution to the acid output and the following relation was assumed:

$$DSLV = CONDH \times (HEAD - HEADMI). \qquad (28)$$

CONDH is a constant. By trial and error methods, a value for CONDH equal to 0.0002 was found to give satisfactory DSLV values. To determine HEADMI, flow and acid data for a given period were compared. During flow periods that give a low and steady acid load, acid load was assumed to be due to diffusion only. The average flow (in inches) during these periods is HEADMI. For Auger Hole #1, such a period occurred between June and July of 1970, and HEADMI = 0.931 inch (or 85 gal/day) was used. The values of HEADMI for the other mines being modeled are listed in Table 14.

WSLOPE: Hypothetical slope of water table. From the point in the K-direction that is flooded, the water table is assumed to rise with slope (WSLOPE). A fixed value for WSLOPE can be assumed and the value of DEHK (described in the next paragraph) can be determined so as to provide enough exposed pyrite material to meet the yearly (or monthly) acid load required. After different values (listed in Table 14) of WSLOPE were used in the development of the model, a fixed value of 0.1 was found to be adequate for use in the models evaluated to date. This is because the variation of WSLOPE has little effect on the acid load removed by inundation.

DEHK: The distance in the K-direction that is flooded. DEHK is calculated by using Eq. (22). In the equation, PER is a constant value so determined that DEHK will have enough exposed pyrite to generate the required yearly acid production. After several trials, a value for PER equal to 1.5 was selected for Auger Hole #1. FLOWMI in Eq. (22) is a constant value which was determined by comparing flow and acid load for a given period. During flow periods that give high acid loads, flooding was assumed to be the major contribution to acid removal. The average flow (in gal/day) during these periods is FLOWMI. For Auger Hole #1, such a period occurred between March and April of 1970, and FLOWMI = 115 gal/day was used.

To summarize; the procedure for modeling a mine by methods proposed in this report may be outlined as follows:

A. Evaluation of Basic Constants and Parameters

  1. Generate daily, monthly, and annual ADD from SUBROUTINE REMOVE

  2. Calculate WSHED and base TANK values

3. Generate daily values of TANK from SUBROUTINE REMOVE
4. Establish relationship between TANK and HEAD
5. Estimate location of water table (i.e., evaluate DEHK).

B. Calculate FLOW and Acid Loads

The required input data are listed as follows:

1. To generate ADD:

   PWHC, PWATER, VAP, and daily weather conditions (AMONTH, IDAY, RAIN, RTIME, TMEAN)

2. To generate TANK:

   In addition to the data required in 1, WSHED, TANK, and CONFH are required

3. To calculate FLOW and acid loads:

   In addition to the data in 1, and 2, NFEET, NLAYER, NDEPTH, NPUNCH, DK, ALKALI, FLOWMI, HEADMI, PER, WSLOPE, DI, TOP, ROCK, TYPE, ALT, REACT, and PYCON are needed.

SECTION XIII

REFERENCES

1. Agnew, A. F., and Corbett, D. M., "Hydrology and Chemistry of Coal Mine Drainage in Indiana," 157th National Meeting, Am. Chem. Soc., Division of Fuel Chemistry, Minneapolis, (1969).

2. Bailey, J. R., "Biological Oxidation of Pyrite," M.S. Thesis, The Ohio State University, (1968).

3. Bird, R. B.; Stewart, W. E.; and Lightfoot, E. N., Transport Phenomena, John Wiley and Sons, New York, (1960).

4. Birle, J. D., "Sulfide to Sulfate Reaction Mechanism in Pyritic Materials," M.S. Thesis, The Ohio State University, (1963).

5. Brown, W. E., "The Control of Acid Mine Drainage Using an Oxygen Diffusion Barrier," M.S. Thesis, The Ohio State University, (1970).

6. Burke, S. P., and Downs, R., "Oxidation of Pyritic Sulfur in Coal Mines," AIMME Transactions, 130 (1938), 425.

7. Caruccio, F. T., "The Quantification of Reactive Pyrite by Grain Size Distribution," Proc. Thrid Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

8. Caruccio, F. T., and Parizek, R. R., "An Evaluation of Factors Affecting Acid Mine Drainage Production in Western Pennsylvania," Proc. Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

9. "Climatological Data, "Environmental Data Service, United States Department of Commerce, (1895-).

10. Corbett, D. M., "Ground Water Hydrology Pertaining to Surface Mining for Coal--Southeastern Indiana," Proc. Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

11. Davis, S. M., and DeWiest, R. J., Hydrogeology, John Wiley and Sons. New York, (1968).

12. Dugan, P. R., and Lundgren, D. G., "Energy Supply for the Chemautotroph Ferrobacillus Ferrooxidans," J. Bact., 89:9 (1965), 825.

13. Good, D. M., "The Relation of Refuse Pile Hydrology to Acid Production," M.S. Thesis, The Ohio State University, (1970).

14. Grove, D. R., "Ferric Ion Oxidation of Pyrite," M.S. Thesis, The Ohio State University, (1970).

15. Jutte, R. B., Jr., "Effect of Oxygen and Nitrogen in Aqueous Solution on the Kinetics of the Sulfide to Sulfate Reaction," M.S. Thesis, The Ohio State University, (1966).

16. Kim, H. W., "Vapor Phase Oxidation of Pyrite," M.S. Thesis, The Ohio State University, (1964).

17. Konicek, M. G., "The Biological Oxidation of Pyrite," M.S. Thesis, The Ohio State University, (1966).

18. Larez, A. L., "Kinetics of Pyrite Oxidation," M.S. Thesis, The Ohio State University, (1970).

19. Lau, C. M.; Shumate, K. S.; and Smith, E. E., "The Role of Bacteria in Pyrite Oxidation Kinetics," Proc. Third Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1970).

20. Lorenz, W. C., and Tarpley, E. C., "Oxidation of Coal Mine Pyrites," United States Bureau of Mines Report of Investigations No. 6247,

21. "Mine Drainage Abstracts; A Bibliography," Coal Research Board, Pennsylvania Department of Mines and Mineral Industries, Bituminous Coal Research, Inc. (1965-   ).

22. Moeb, N. N., "Mine Air Sealing: A Progress Report" Proc. Second Symposium on Coal Mine Drainage, Mellon Inst. Pittsburgh, Pa., (1968).

23. Morth, A. H., "Reaction Mechanism of the Oxidation of Iron Pyrite," M.S. Thesis, The Ohio State University, (1965).

24. Morth, A. H., and Smith, E. E., "Kinetics of the Sulfide-to-Sulfate Reaction," 151st National Meeting, Am. Chem. Soc., Pittsburgh, Pa., (1966).

25. Morth, A. H., "Acid Mine Drainage: A Mathematical Model" Ph.D. Dissertation, The Ohio State University, (1971).

26. Moulton, E. Q., "The Acid Mine Drainage Problem in Ohio," Engineering Experiment Station, Bulletin 166, The Ohio State University, (1957).

27. Ohio State University Research Foundation, "Sulfide to Sulfate Reaction Mechanism," Water Pollution Control Research Series 14010 FPS--02/70, Federal Water Quality Administration, Department of Interior, (1970).

28. Nelson, H. W.; Snow, R. D.; and Keyes, D. B., "Oxidation of Pyritic Sulfur in Bituminous Coal," IEC, 25 (1933), 1355.

29. Sasmojo, S., "Oxidation Kinetics of Pyritic Materials in Aqueous Media," Ph.D. Dissertation, The Ohio State University, (1969).

30. Scott, R. B.; Hill, R. D.; and Wilmoth, R. D., "Cost of Reclamation and Mine Drainage Abatement-Elkins Demonstration Project," 14010--10-70, Water Quality Office, Environmental Protection Agency, (1970).

31. Shumate, K. S., and Smith, E. E., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Proc. Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

32. Shumate, K. S., Associate Professor, The Ohio State University, Personal Communication.

33. Shumate, K. S.; Smith, E. E.; and Brant, R. A., "A Model for Pyritic Systems," 157th National Meeting, Am. Chem. Soc., Division of Fuel Chemistry, Minneapolis, Minn., (1969).

34. Singer, P. C., and Stumm, W., "Oxygenation of Ferrous Iron in Mine Drainage Waters," 157th National Meeting, Am. Chem. Soc., Division of Fuel Chemistry, Minneapolis, Minn., (1969).

35. Smith, E. E., Professor, The Ohio State University, Personal Communication.

36. Smith, E. E., "Engineering Aspects of Acid Mine Drainage," Proc. Second Annual Symposium, Water Resources Research, The Ohio State University, (1966).

37. Smith, E. E., and Shumate, K. S., "Pilot Scale Study of Acid Mine Drainage," Water Pollution Control Research Series 140.0 EXA 03/71.

38. Smith, E. E.; Svanks, K.; and Halko, E., "Aerobic-Anaerobic Oxidation of Pyrite," 157th National Meeting, Am. Chem. Soc., Division of Fuel Chemistry, Minneapolis, Minn., (1969).

39. Smith, E. E.; Svanks, K.; and Shumate, K. S., "Sulfide to Sulfate Reaction Studies," Proc. Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

40. Sternberg, Y. M. and Agnew, A. F., "Hydrology of Surface Mining--A Case Study," Water Resources Res., 4:2, (1968), 363-8.

41. Stiles, D., Unpublished Data, The Ohio State University.

42. Thornthwaite, C. W., and Mather, J. R., "Instructions and Tables for Computing Potential Evapotranspiration and the Water Balance," Publications in Climatology, Volume X, Number 3, Drexel Institute of Technology Laboratory of Climatology, Centerton, New Jersey (1957).

43. Vimmerstedt, J. P., and Struthers, P. H., "Influence of Time and Precipitation of Chemical Composition of Spoil Drainage," Proc. Second Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., (1968).

44. Wisler, C. O., and Brater, E. F., Hydrology, John Wiley and Sons, New York (1959).

SECTION XIV

LIST OF PUBLICATIONS

1. Morth, A. H.; Smith, E. E.; and Shumate, K. S., "Pyritic Systems: A Mathematical Model," 3rd Symposium on Coal Mine Drainage, Mellon Inst., Pittsburgh, Pa., May 1920, 1970.

2. Morth, A. H., "Acid Mine Drainage: A Mathematical Model," Ph.D. Dissertation, The Ohio State University (1971).

3. Chow, K. Y. "Computer Stimulation of Acid Mine Drainage," M.S. Thesis, The Ohio State University (1972).

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